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ON OSARIZAWAITE, A NEW MINERAL OF THE ALUNITE GROUP, FROM THE OSARIZAWA MINE, JAPAN*

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ABSTRACT

Osarizawaite, a new mineral, from the Osarizawa mine occurs in the oxidized zone of lead-zinc-copper veins as earthy and friable masses, associated with other secondary minerals of lead or copper. The chemical formula of osarizawaite has been determined as Pb $(Cu_{0.98}\ Zn_{0.02})$ $(Al_{0.81}\ Fe_{0.19})_2$ $(SO_4)_2$ $(OH)_6$. Its physical and optical properties are: greenish-yellow in colour; specific gravity=3.89~4.02, 4.20 (calc.); mean index of refraction=1.735~1.757, birefringence strong. The unit cell dimensions for both the hexagonal cell and the corresponding rhombohedral cell are: a_0=7.05Å., c_0=17.23Å., Z=3; a_{rh}=7.04Å., α=60°06′, Z=1. The data obtained demonstrate that the mineral is a new species being the aluminum analogue of beaverite and belongs to the alunite group. A new mineral name, osarizawaite, is proposed for the mineral which belongs to the alunite group and whose ideal chemical formula is $PbCuAl_2(SO_4)_2(OH)_6$ where Cu and Al may be partially replaced by Zn and Fe respectively.

Introduction

Oxidized zones fairly large scale have been found at the shallow parts of lead-zinc-copper veins among the Shôtoku and Utori vein groups which are situated in the north-eastern part of the mineralized area of the Osarizawa mine. The oxidized zone, which is lately exploited, contains various secondary minerals of lead and copper. The main constituent minerals are anglesite and limonite. They are accompanied by an unknown mineral which is greenish-yellow in colour

* Read at the Annual Meeting of the Mineralogical Society of Japan held in Tokyo on June 2, 1961.

and occurs in powdery or earthy masses. The writer studied the specimens of this mineral collected from the Shôtoku 6b-2 Vein, and identified it to be a new species of the composition $Pb\ (Cu_{0.98}\ Zn_{0.02})\ (Al_{0.81}\ Fe_{0.19})_2\ (SO_4)_2\ (OH)_6$.

In this paper the writer will present a brief explanation of the occurrence and the results of examinations on the new mineral, which is named "osarizawaite" after the name of the locality.

Occurrence and paragenesis

The Osarizawa mine, one of the most famous copper mines in Japan, is located in the north-eastern part of Akita Prefecture. The ore deposits consist of about four hundred veins cutting the Miocene green tuff and silicious shale complex and the augite andesite and plagio-liparite which are intruded into the complex.

The Shôtoku and Utori vein groups are situated in the north-eastern part of the Osarizawa mining area and composed of epithermal veins filling the numerous fissures of E.-W. system distributed near the two main faults "Higashi" and "Nishi", striking NE. Most of them are simple chalcopyrite-pyrite veins similar to other deposits of the Osarizawa mine, but some of them, Shôtoku 6b Vein or Utori 2 Vein in which osarizawaite occurs, are characterized by oxidized zone of considerable scale and downward they gradually pass into chalcopyrite-pyrite zone through galena-sphalerite zone. Those oxidized zones are directly bordered on the Higashi or Nishi Fault and their boundaries on other sides are controled by the accessory small faults.

The oxidized zones chiefly consist of anglesite and limonite, and the following secondary minerals have been also recognized: linarite, azurite, brochantite, malachite, chalcocite, covellite, sulphur, chalcedony, kaolinite and hydrous oxides of manganese.

Anglesite occurs forming intermittent, branch-rich veinlets or small ring ores in the limonitized vein and in some places it includes galena as nucleus.

In general, linarite, azurite, brochantite and malachite are distributed only locally, running along or somewhat standing away from the anglesite veinlets, and rarely accompanied by black manganese mineral.

Chalcocite and covellite are also found locally in limonitized vein as sweet-potato-shaped blocks of which a small quantity of galena, sphalerite, chalcopyrite and pyrite remains at the central part.

Dotty sulphur is found at times in a cavity of strongly bleached rock.

Osarizawaite occurs as a powdery or earthy crust on the surface or in the crack or cavity of the aggregate of anglesite, limonite and other associated minerals above described. It does not form a distinctive veinlet or massive aggregate, but it is clearly distinguished from the associated minerals by its characteristic colour, namely the Japanese bushwarbler colour (greenish-yellow). Although this mineral has been recognized macroscopically in small quantities only at a part of the upper second level of Shôtoku 6b-2 Vein and the upper third level of Utori 2 Vein, there is a possibility of more extensive distribution in the microscopic order.

The osarizawaite crystals collected for this study from the Shôtoku Vein were so fine that no crystal form has been recognized with the naked eye or even with a magnifying glass. Under the microscope, the mineral occurs, in some cases, on the surface of porous mother rock mainly consisting of kaolinite accompanied by quartz, limonite etc. In other cases, it occurs surrounding anglesite or along the cracks of anglesite which occurs abundantly filling the interstitial spaces of vein-quartz.

Most of osarizawaite crystals form such close masses that it was impossible to discriminate single crystals even under the microscope, but some of the scattered grains are often crystallized in distinct hexagonal outline and appear to be composed of pyramidal faces at terminal (Figs. 1~4, Plates I and II).

Preparation of materials

The materials for the study were milled so as all the products passed through the 200 mesh screen and then osarizawaite in the +270 mesh fraction was purified by means of a super-panner and a Frantz isodynamic magnetic separator. In those processes, microscopic observation, spectrographic analysis and X-ray powder diffraction analysis were used to certify the purity of the products. As the result of those treatment, the osarizawaite concentrate free from the accompanying minerals was obtained. It was confirmed under the microscope that the concentrate contained only very small amounts of quartz which were stained partly with limonite or locked with osarizawaite and was not contaminated with any other transparent or opaque mineral at all (Fig. 4, Plate II).

Physical properties

The mineral is a greenish-yellow earthy looking material and the mass is so friable as easily crushed between fingers. The specific gravity was determined as 3.89~4.02 with a pycnometer using distilled water and removing bubbles by a vacuum pump. The specific gravity as calculated from the chemical composition and the unit-cell dimensions which are to be described later is 4.20. The discrepancy between these values is rather large, but explanation might possibly be found in the very fine-grained and closely coagurated nature of osarizawaite.

Osarizawaite is greenish-yellow or yellowish-green in thin section. The fine-grained character of the mineral precludes the measurement of any optical property other than the mean index of refraction. Measurements made on several specimens by means of immersion method yielded the mean index of refraction ranging from 1.735 to 1.757 for white light, and such tendency was perceptible that the more green-tinged grains have lower mean index. The birefringence is respectably high.

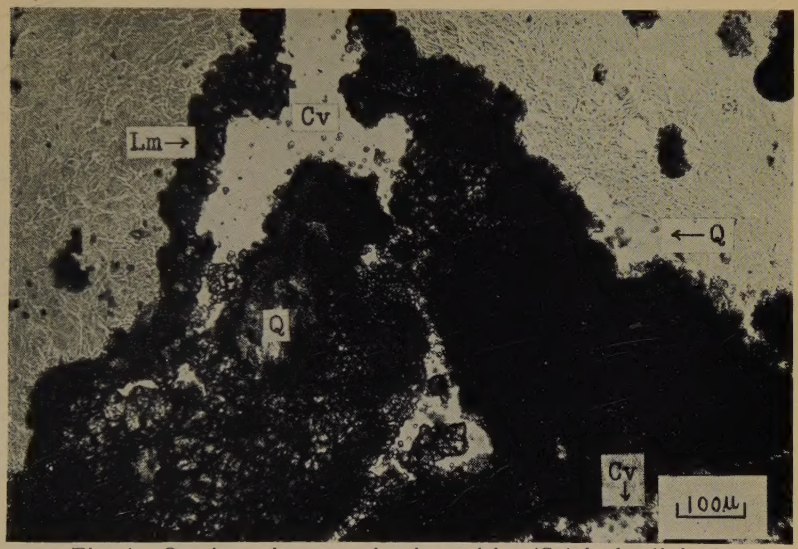

Fig. 1. Osarizawaite occurring in cavities (Cv) in kaolinized rock (pale grey). Limonite (Lm) covers the wall of cavity which in turn is covered by osarizawaite. Q=quartz.

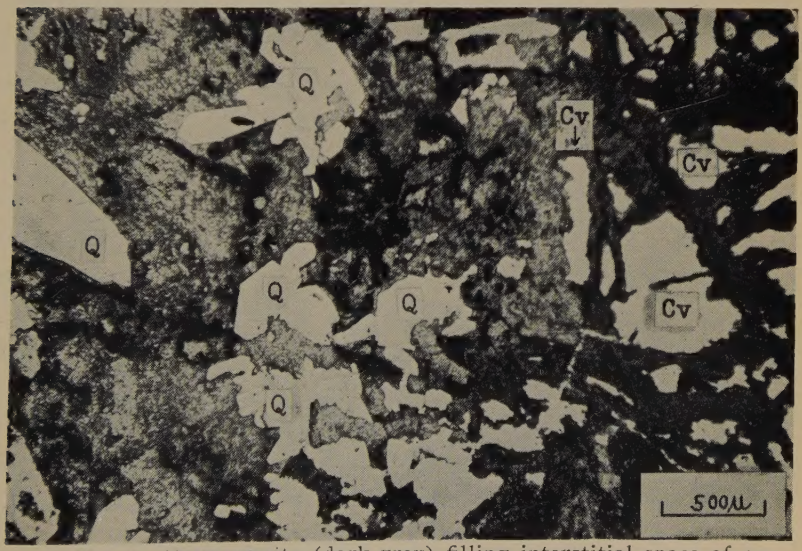

Fig. 2. Osarizawaite (dark grey) filling interstitial space of anglesite (pale grey) crystallized around vein-quartz (Q). The grey area on the right rich in cavity is an aggregate of very fine-grained osarizawaite.

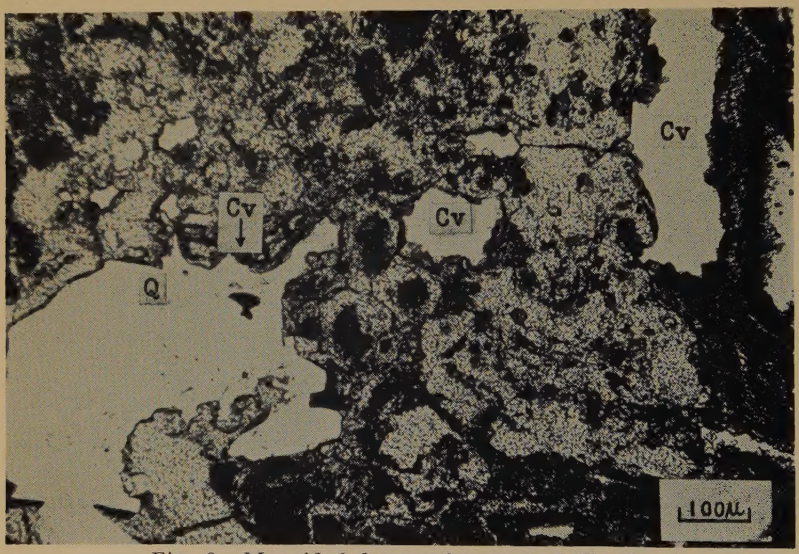

Fig. 3. Magnified figure of a part of Fig. 2.

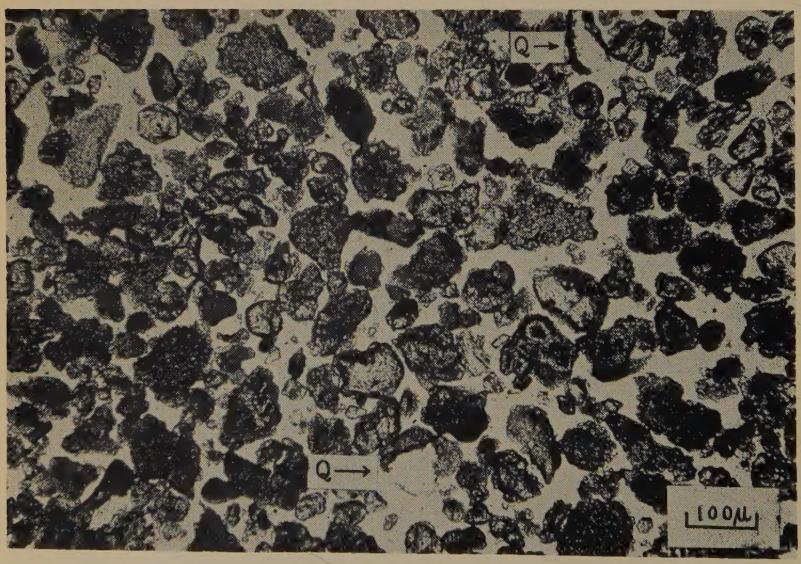

Fig. 4. Concentrate of osarizawaite.
A quartz (Q) grain at lower part is locked with osarizawaite, and one at upper part is stained partly with limonite. All the others are osarizawaite. At upper-left part or other several places, hexagonal outline of osarizawaite is recognized.

Radioactivity was not recognized.

Chemical properties

The mineral is insoluble in water and practically shows no reaction to nitric acid. Only the boiling concentrated hydrochloric or sulphuric acid disintegrates the mineral perfectly and precipitates lead chloride or lead sulphate. Also, the mineral is almost insoluble in the boiling ammonium acetate solution (Huffman's method)[3].

The standard procedures of chemical analysis were employed for each components except water. Total water was determined by the absorption method heating at 500°±10°C. The limitation of the temperature and the division of the total water into $H_2O(+)$ and $H_2O(-)$ were based on the dehydration test later described.

The result of the chemical analysis on the prepared concentrate is shown in Table 1. The presence of SiO_2 is caused by a small amount of quartz as were recognized under the microscope. The zinc may be a minor substituent for copper, judging from the similarity of ionic radii (Zn^{2+}=0.83, Cu^{2+}=0.83)[2], although in sulphate minerals such a illustrative instance has not yet been known as in some carbonates or phosphates, for instance, the relation between malachite and zincrosasite[7] or the substitution in veszelyite. The source of CO_2 was not ascertained, because no carbonate mineral was recognized in the concentrate under the microscope, in spite of the possibility of contamination of the accompanying carbonate minerals.

A qualitative spectrographic analysis of the mineral showed the presence of Mn and Ag in thousandths or less of one per cent.

By the result shown in Table 1, osarizawaite conforms to the formula $Pb(Cu_{0.98}Zn_{0.02})(Al_{0.81}Fe_{0.19})_2(SO_4)_2(OH)_6$. This formula resembles that of beaverite $PbCu(Fe_{0.75}Al_{0.25})_2(SO_4)_2(OH)_6$ described in "Dana's The System of Mineralogy"[5] (abbreviated to "Dana" hereafter), but there is a remarkable contrast between them in the ratio of Al to Fe.

Table 1. Chemical composition of osarizawaite.

	Wt. %	Mol. prop.	Mol. rat.		Recalc.	Ideal
PbO	32.72%	0.1466		1.02	35.41%	35.45%
CuO	11.27	0.1417	0.99	1.01	12.20	12.40
ZnO	0.22	0.0027	0.02		0.24	0.24
Fe_2O_3	4.43	0.0277	0.19	1.04	4.79	4.72
Al_2O_3	12.35	0.1211	0.85		13.36	13.18
SO_3	22.92	0.2862		2.00	24.80	25.43
SiO_2	2.18					
As	0.00					
CaO	0.00					
MgO	0.00					
CO_2	0.45					
$H_2O(+)$	8.50	0.4717		3.30	9.20	8.58
$H_2O(-)$	4.05					
Total	99.09%				100.00%	100.00%

Recalc.: Recalculated to 100% after deducting impurities.
Ideal: Ideal $Pb(Cu, Zn)(Al, Fe)_2(SO_4)_2(OH)_6$ in which CuO/ZnO=1417/27 and Fe_2O_3/Al_2O_3=277/1211.

X-ray data

X-ray powder diffraction patterns of osarizawaite were taken under the operating conditions as follows:

X-ray radiation: Cu$K\alpha$ (Ni-filtered), 35kV., 10mA.
Scale factor: 16, multiplier: 1, time constant: 4 sec., divergence slit: 2½°, receiving slit: 0.2 m/m, scatter s it: 2½°, scanning speed: 1°/min.

The X-ray powder lines* are listed in Table 2. On the basis of its crystal form under the microscope and its similarities to beaverite in chemical composition, the indexing of the reflections of the mineral

* The data obtained independently by T. Watanabe and A. Kato, on the fraction of the same material showed good agreements in *d*-spacings within the range of ±0.003 and in unit cell dimensions, a_0=7.05Å., c_0=17.22Å., with the writer's results.

Table 2. X-ray powder data for Osarizawaite.

h k l	*I*	$d_{obs.}$	$d_{calc.}$*
0 0 3 1 0 1	70	5.79Å	5.74Å 5.75
0 1 2	5	4.98	4.98
1 0 4, 1 1 0	60	3.52	3.52
0 1 5, 1 1 3	100	3.00	3.00
0 0 6 2 0 2	60	2.87	2.87 2.88
0 2 4	20	2.49	2.49
1 0 7 2 0 5, 1 2 1	60	2.28	2.28 2.29
1 1 6, 1 2 2	30	2.23	2.23
2 1 4, 0 1 8, 3 0 0	10	2.03	2.03
0 0 9 0 2 7 1 2 5 0 3 3	30	1.918	1.915 1.916 1.917 1.918
2 0 8 2 2 0	20	1.762	1.760 1.762
1 1 9 2 1 7 2 2 3, 1 3 1	20	1.683	1.682 1.683 1.685
1 0 10 0 3 6 3 1 2	5	1.660	1.658 1.660 1.661
0 1 11 3 1 5, 4 0 1	10	1.519	1.517 1.520
0 2 10 2 2 6 0 4 2	30	1.500	1.501 1.502 1.503
0 0 12 4 0 4	5	1.436	1.436 1.439
2 0 11, 0 3 9 1 3 7 0 4 5, 3 2 1	10	1.397	1.394 1.395 1.396
1 1 12 3 1 8 3 2 4, 1 4 0	5b	1.332	1.330 1.331 1.332
1 0 13 1 2 11 2 2 9, 4 0 7 2 3 5, 1 4 3	10b	1.298	1.295 1.296 1.297 1.298

* Calculated on the basis of a_0=7.05Å., c_0=17.23Å.

was carried out on the assumption that the mineral is a member of the rhombohedral system and referring to that of hidalgoite[6]. The unit cell dimensions thus obtained for both the hexagonal cell and the corresponding rhombohedral cell are: $a_0=7.05$Å., $c_0=17.23$Å., $c_0/a_0=2.44$, $Z=3$; $a_{rh}=7.04$Å., $\alpha=60°06'$, $Z=1$. Calculated d-spacings from these parameters are in good agreement with the measured values as shown in Table 2, and the indices satisfy the equation $-h+k+l=3n$, which is the prerequisite to the conventional setting of the rhombohedral cell indexed on hexagonal axes. Thus, this X-ray powder data may admit the mineral to be a member of rhombohedral system. On the other hand, the tendency that each reflection corresponds to two or three indices strongly indicates the pseudo-isometric charactor which is one of the common features of the alunite group.

Thermal analyses

(1) *Dehydration test*

The loss of weight of osarizawaite on heating was measured using 200 mg. of the material. The result shown in Fig. 5 was obtained after the corrections of errors which might be caused by buoyancy or convection of air on high temperature, referring to the blank test. The material was free from an absorbed or adhered water as it had been stored in a decicater for a certain time.

As shown in Fig. 5, no water is driven off upto about 400°C. in effect. At above 400°C. the losses in weight take place in three or four steps, i.e., the abrupt and distinct changes at about 400°, 600° and 850°C. and another obscure small step at 750°~800°C. This obscure step is exposed more distinctly in the differencial thermal analysis curve mentioned later.

Since the figure of loss of weight at about 400°C. approximately coincides with the content of $H_2O(+)$ measured by absorption method, it is doubtless that the first step of weight loss is the result of the dehydration of crystal water. The losses at about 600°C. and the higher temperatures are derived from expelled SO_3, that was con-

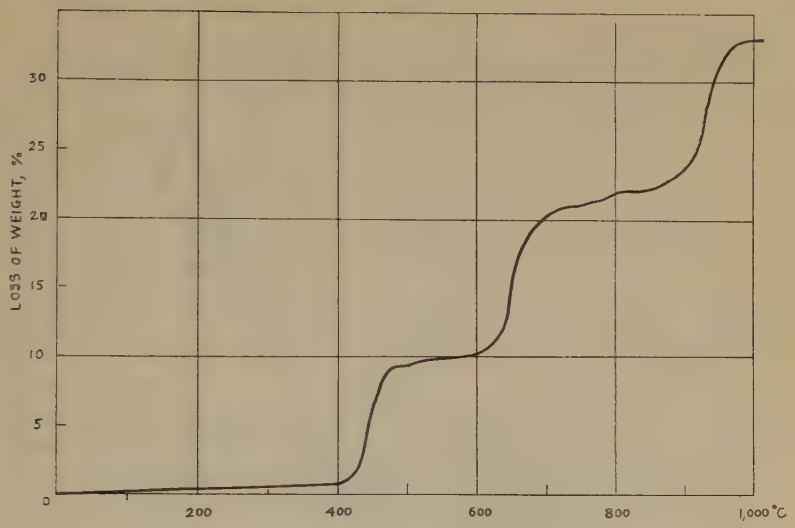

Fig. 5. Dehydration curve of osarizawaite.
Heating rate: 2°C/min. Thermo-balance: Ôshima-Fukuda M.

firmed by the rising of white smoke as well as by the detection of SO_4 ions in the distilled water after it was used to wash the dew-drops stuck on the quartz wire or the inside wall of the glass tube of thermobalance.

Therefore, the mineral is considered to decompose through the process of dehydration at about 400°C. and of expelling SO_3 at about 600° and 850°C.

(2) *Differential thermal analysis*

The differential thermogram of osarizawaite is given in Fig. 6.

The material was left as it was in room. In Fig. 6, a small endothermic peak at 100°C. may be caused by dehydration of the absorbed water, and compared with the dehydration curve, a remarkable endothermic peak at 460°C. is due to the dehydration of crystal water, while the endothermic peaks at 760° and 1,000°C. are due to vaporization of SO_3. The cause of the endothermic peak at 830°C. which may correspond with the obscure step between 750° and 800°C.

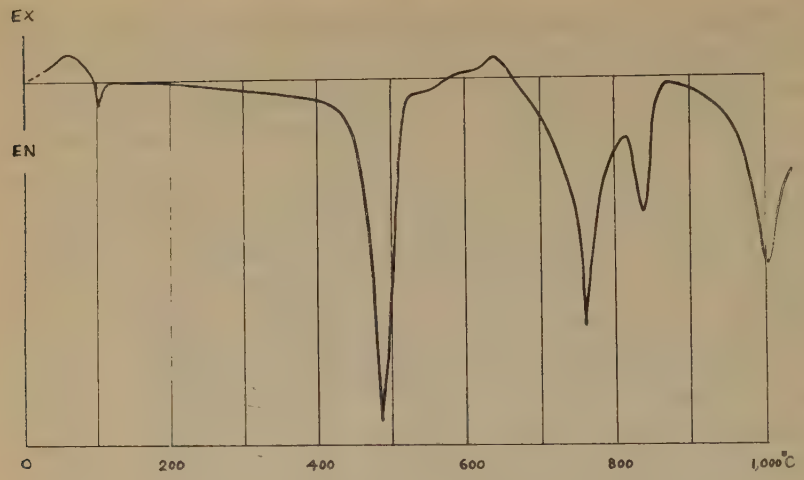

Fig. 6. Differential thermal analysis curve of osarizawaite. Heating rate: 10°C/min.

in the dehydration curve has not been ascertained, because nothing that may invite the peak was present in the material inferring from the results of microscopic observation or chemical analysis. This suspectable peak may be due to a previous and partial expulsion instead of whole expulsion of SO_3 at one stroke. The question will be left for further study, for instance, X-ray analysis of the product after heating at each definite temperature.

An exothermic curve below 100°C. is caused by insufficient adjustment of the apparatus, but a small exothermic peak at about 640°C. preceding the first expulsion of SO_3 is considered to be caused by transition of Al_2O_3 to α-Al_2O_3 as recognized in the d.t.a. curve of alunite[4].

Comparison of osarizawaite with beaverite

The properties of osarizawaite above described are summarized in Tables 3 and 4 comparing with those of beaverite.

There is striking resemblance between their chemical compositions, namely the molecular ratios of their components except Fe_2O_3

Table 3. Chemical compositions of osarizawaite and beaverite.

	Osarizawaite		Beaverite 1		Beaverite 2	
	Wt. %	Mol. rat.	Wt. %	Mol. rat.	Wt. %	Mol. rat.
PbO	35.41%	1.02	33.71%	1.00	32.50%	1.00
CuO	12.20	0.99 } 1.01	12.02	1.00	10.74	0.92
ZnO	0.24	0.02 }				
Fe_2O_3	4.79	0.19 } 1.04	18.08	0.75 } 1.00	19.13	0.82 } 1.09
Al_2O_3	13.36	0.85 }	3.85	0.25 }	4.03	0.27 }
SO_3	24.80	2.00	24.18	2.00	23.60	2.02
$H_2O(+)$	9.20	3.30	8.16	3.00	10.00	3.80
Total	100.00%		100.00%		100.00%	

Osarizawaite: Recalculated to 100 after deducting impurities.
Beaverite 1: Ideal Pb $(Cu, Fe, Al)_3 (SO_4)_2 (OH)_6$ with Cu : Fe : Al = 2 : 3 : 1 (after Dana[5]).
Beaverite 2: Beaver County, Utah. After deducting 10.05% insol. and recalculating to 100 (after Butler and Schaller[1]).

Table 4. Physical and optical properties of osarizawaite and beaverite.

	Osarizawaite	Beaverite ("Dana"[5])
Crystal system	hexagonal-R, pyramidal (?)	hexagonal-R, ditrigonal-pyramidal*
Space group	——	R3m
a_0	7.05Å.	7.203Å.
c_0	17.23Å.	16.94 Å.
c_0/a_0	2.444	2.351
Habit	earthy and friable masses	earthy and friable masses
Colour	greenish-yellow	canary-yellow
Specific gr.	3.89~4.02, 4.20 (calc.)	4.36, 4.31 (calc.)
Optical prop.	——	uniaxial negative
	n=1.735~1.757	ω variable, 1.85±0.02
	birefringence strong	birefringence strong
Solubility	insol. in water, HNO_3, $NH_4C_2H_3O_2$,	insol. in water
	sol. in HCl or H_2SO_4 (conc, boil)	sol. in HCl (boil)

* Crystals of beaverite have not been measured. X-ray powder diffraction patterns show that it is rhombohedral and has cell dimensions close to those of other minerals of the alunite group. For this reason it is assigned to the ditrigonal-pyramidal class ("Dana"[5]).

and Al_2O_3 are much the same. The content of H_2O in beaverite will be discussed later. Only the ratio of Fe_2O_3 and Al_2O_3 is reversed between them. On the other hand, as shown in Table 4, there are respectable differences between them in the unit cell dimensions, colour, specific gravity and mean index of refraction, in spite of the resemblance of their crystallographic genealogies, modes of occurrence* or other general properties. The similar relation is found between jarosite and alunite which belong to the same group as beaverite. In regard to the unit cell dimensions, osarizawaite resembles alunite (a_0=6.96Å., c_0=17.35Å.) in contrast to the close approximation of beaverite to jarosite (a_0=7.20Å., c_0=17.00Å.). Accordingly, the differences in physical and optical properties between osarizawaite and beaverite are considered to be caused by the remarkable contrast of ratios of Fe_2O_3 to Al_2O_3.

Beaverite has been reported by B. S. Butler and W. T. Schaller[1] in 1911 as a new mineral produced from the Horn Silver mine in Beaver County, Utah, and according to their original paper, it is a name given for a mineral that have the idealized chemical formula of $CuO \cdot PbO \cdot Fe_2O_3 \cdot 2SO_3 \cdot 4H_2O$ in which the copper and lead are assumed to exist in equal molecular amounts and a little ferric iron is replaced by alumina, or the formula can be written more exactly as $4CuO \cdot 4PbO \cdot 3Fe_2O_3 \cdot Al_2O_3 \cdot 8SO_3 \cdot 16H_2O$ following to their chemical analysis. But there are some confusions regarding to the expression of the chemical formula. Namely it is described as $Pb\,(Cu, Fe, Al)_3\,(SO_4)_2\,(OH)_6$ in the "Dana"[5] or as $[PbCu\,(Fe, Al)_2\,(SO_4)_2\,(OH)_6 \cdot H_2O\,?]$ by A. N. Winchell[8], although both of them were derived from the data in the original paper.

The formula shown by original authors is also applicable to that by Winchell, and it has just one molecule of H_2O in excess compared with the formula in the "Dana". The authors gave the figure of

* The minerals associated with osarizawaite have also been recognized with beaverite by Butler and Schaller[1].

molecular ratio 3.8 to $H_2O(-)$ of beaverite as the result of their analysis as shown in Table 3, but the accuracy of the figure seems to be still open to question, because the authors themselves noticed experimental accident in their paper. Taking the result of the writer's study on osarizawaite into consideration, $3H_2O$ (or 6OH) may be appropriate to the crystal water of beaverite as described in the "Dana".

The components of Cu, Fe and Al in beaverite are lumped together as $(Cu, Fe, Al)_3$ in the "Dana"[5], while by Winchell[8] as $Cu(Fe, Al)_2$. The replacement between Cu^{2+} and Fe^{3+} or Al may be very difficult according to the differences between their ionic radii or their behaviors as metallic ion. In fact, such an instance has not been known. Furthermore, the lead and copper are equal in molecular ratio in osarizawaite, as well as in beaverite, while the ratios of ferric iron and aluminum are reversed. Taking those facts into consideration, it may be reasonable to express the relation of Cu, Fe and Al in the formula of beaverite as $Cu(Fe, Al)_2$ after the description by Winchell.

Referring to beaverite, the chemical formula of osarizawaite should be shown as $PbCu(Al, Fe)_2(SO_4)_2(OH)_6$ or could be written as $PbCuAl_2(SO_4)_2(OH)_6$ corresponding to the idealized formula of beaverite. The two minerals are inferred to form a subgroup in the alunite group characterized by lead and copper. The distinction between beaverite and osarizawaite is essentially made in ferric iron and aluminum contents, the former corresponding to jarosite, while the latter to alunite.

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PARAGENESES OF THE MINERALS OF THE NINGYÔ-TÔGÉ MINE

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Abstract

In the Ningyô-tôgé area, uranium is emplaced in the Neogene basal conglomerate deposited on the eroded surface of the Mesozoic granite. The geological environment of the uranium ores is similar to the general sandstone type uranium deposits, but the mineralogy is peculiar in some respects. Three uranium minerals, ningyoite, autunite and uraninite have been identified in the mine, and besides them humic acid, limonite and biotite were found to be uraniferous. Most of the uranium in the ores is contained principally in ningyoite in the unoxidized zone, and in autunite in the oxidized zone. Uranium of the other forms occurs rather locally or less abundantly.

The ores are mostly composed of allogenic rock forming minerals and their altered products. Authigenic minerals, though they are less in the amounts than the allogenic minerals, occur commonly coating pebbles or mineral grains, filling cavities, and replacing allogenic minerals. These are kaolinite, chlorite, montmorillonite, carbonaceous matter, marcasite, pyrite, sphalerite, gypsum, melanterite, uranous minerals, sericite, calcite, siderite, limonite and uranyl minerals, roughly in the order of the formation. The last four minerals are found only in the oxydized zone. Part of the authigenic minerals appears to have been formed during the diagenesis and the others were precipitated from or altered by the extrinsic solution. The correlation analysis revealed that uranium is associated with P, S, Ca, Zn and As, and the exceedingly good correlation of phosphorus with uranium has been demonstrated. The correlation analysis was applied also for some minerals, which were analyzed quantitatively with X-ray diffractometer. Remarkably good correlation was found between uranium and sericite, and between uranium and gypsum, while the strongly negative correlation was shown between uranium and kaolinite.

These statistical consideration of uranium with some authigenic minerals and elements, together with the paragenetic study of the ores by microscopic observation indicated that uranium was precipitated mostly as ningyoite with gypsum from uranium containing ore solution, which transformed kaolinite partly into sericite during the uranium mineralization.

Introduction

The Ningyô-tôgé uranium mine is located around the boundary between Kamisaibara-mura, Tomada-gun, Okayama Prefecture and Misasa-machi, Tôhaku-gun, Tottori Prefecture. The mine ranges about 7 km. from the east to the west end, and consists of three main ore bodies. They are called Ningyô-tôgé (or Tôgé), Yotsugi and Nakatsugô, from the west to the east. There is another important uranium mine of the similar type called Tôgô mine which is bounded on the south by the Ningyô-tôgé mine. The description, however, will be confined on the ores of the Tôgé and the Yotsugi ore body in the present paper.

The ore deposits belong to the sedimentary type, and the sedimentary features of the country rocks are very similar to those of the so-called sandstone type uranium deposits in many respects. But the ores are very peculiar in mineralogical view point, and most of uranium found in the unoxidized zone of the deposits is contained in a new mineral, ningyoite. This paper aims to describe the mineralogy of the ores with special reference to the paragenetic relation between uranium and the authigenic minerals in the unoxidized zone.

Outline of the ore deposits

Base rocks around the ore deposits are mostly Cretaceous granite (medium to coarse grained biotite granite), Palaeozoic metamorphic rocks, and various volcanic rocks which are metamorphosed at the contact with the granite and is called Kijiyama volcanic complex. These base rocks, which were suffered from peneplanation, are overlain by Neogene sediments (probably early pliocene) and subsequent lava flows of dacitic to basaltic rocks. The sediments comprise fluvial to lacustrine Nigyô-tôgé formation and volcanic debris, Takashimizu or Nakatsugô formation. There are younger formations (partly belonging to the Daisen formation) consisting of tuffaceous sand stone and conglomerate in some places of the area.

The ore deposits are distributed almost horizontally at about 720 m. above the sea level. Uranium occurs mostly in the basal conglomerate of the Ningyô-tôgé formation, which consists of irregularly alternated sandstone, mud stone, and conglomerate with thickness attaining about 60 m. The thickness of the basal conglomerate is about two to three metres, and it comprises subangular or subrounded cobbles of granite, andesitic rocks including plagioliparite, dacite, porphyrite and tuff breccia, and Palaeozoic metamorphic rocks. Occasionally, the pebbles become very small in their sizes, and it is better called as arkose sandstone. Some of the uranium, however, is contained also in the upper beds of alternated mudstone and sandstone, especially in the Nakatsugô ore body.

The ores are found to be oxidized where the overburden is thinner (probably less than 10 to 20 m.), or along faults. Vertically uranium tends to enrich in lower part of the conglomerate, in both unoxidized and oxidized zone. Horizontal variation of the uranium contents of the ores is attributed mostly to the undulation of the unconformity plane between the granite and the conglomerate as shown in Fig. 1. The high grade ores are mostly confined in troughs, especially around junctions of two troughs (e.g., Drift No. 2-100~130 m.). There are some faults which cut the conglomerate, and part of them is associated with higher grade ores around themselves, though the uranium contents of the fault breccias are generally low. The uranium contents of the mudstone just above the basal conglomerate are also comparatively high near these faults.

Uranium is mainly contained in the matrices of the conglomerate as indicated by the sizing analyses[15]. Most pebbles are less uraniferous, although surface of the pebbles are similarly uraniferous as the matrices.

Details of the geology and the ore deposit should be refered in other papers[11) 12) 15) 24) 25)].

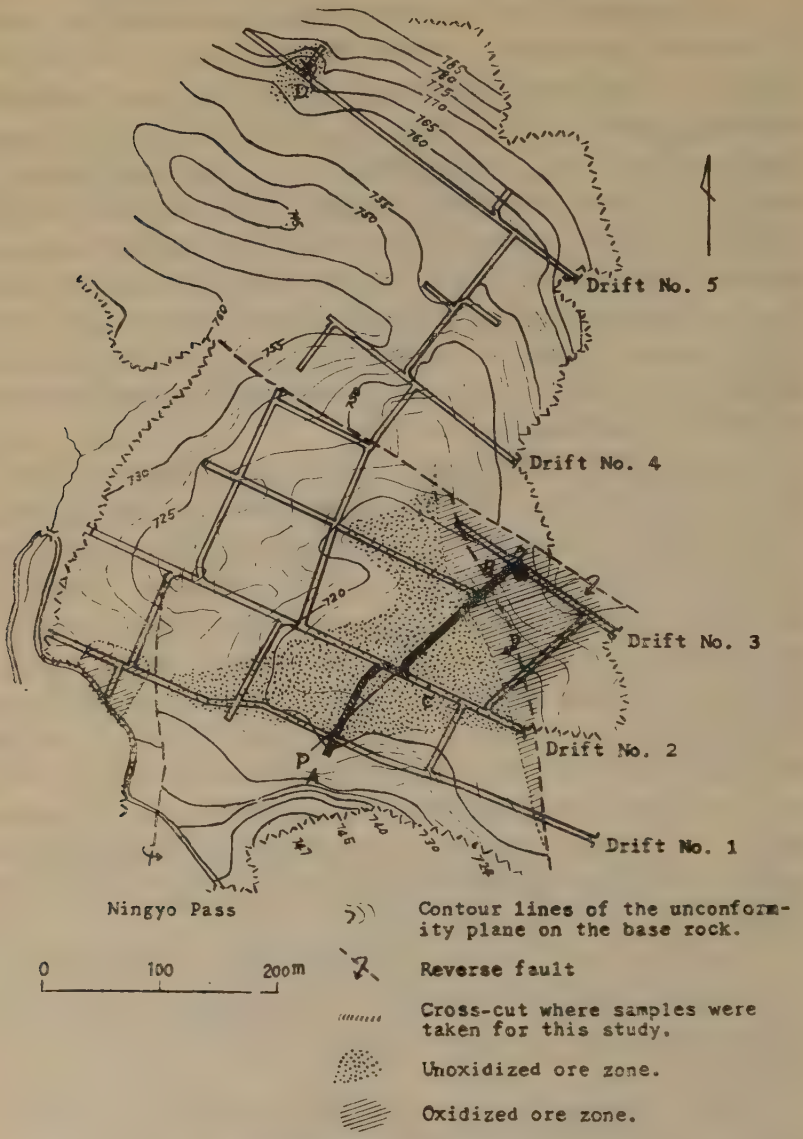

Fig. 1. Contour map showing the unconformity plane on the base rock in the Tôgé area.
After a map drawn by Ningyô-tôgé Branch, Atomic Fuel Corporation.

Mineral composition of the ores

The uranium ores of the Ningyô-tôgé mine are classified into two kinds, unoxidized ores and oxidized ores. They occur generally separated in the deposits, but the intermediate ore is seen in the transitional zone. The unoxidized ores are grey to black in colour, and the oxidized ores are yellowish grey to brown. The chemical composition of the ores chiefly depends on the constituents of the country rocks or of the pebbles. Table 1 shows an example of the chemical composition of the ore. The major components are very similar to common granodiorite except for uranium and zinc.

Table 1. Chemical analysis of a high grade ore.

SiO_2	66.25%
Al_2O_3	15.24
Fe_2O_3	5.25
TiO_2	0.46
CaO	1.47
MgO	0.42
Na_2O	2.40
K_2O	3.36
ZnO	0.12
CuO	—
U_3O_8	0.50
Ign. loss	3.76
Total	99.23%

Analyst: T. Muto.
The sample was taken from Drift No. 2-130 m. in the unoxidized zone of the Tôgé ore body.

The ores are mostly composed of common rock forming minerals of allogenic origin and their altered products. The principal minerals are quartz, potash-feldspars and kaolinite where the country rock consists of mostly disintegrated materials of granite, and plagioclase and montmorillonite where it consists of mainly andesitic rocks. The authigenic minerals are uranium minerals, sulphides, sulphates, iron oxides, a part of clay minerals, and so on. They seem to have important relation to the uranium mineralization, though their amounts are comparatively small. Table 2 shows the mineral composition of the ores of the Tôgé ore body with the order of their contents estimated with microscope and X-ray.

Table 2. Mineral composition of the ores.

Allogenic mineral	Content (%)	Authigenic mineral	Content (%)
Quartz	15～50	Pyrite	tr.～5
K-feldspars	10～40	Marcasite	tr.
Plagioclase	10～40	Sphalerite	tr.
Biotite	1～ 3	Gypsum	tr.～5
Muscovite	tr.	Melanterite	tr.
Hornblende	1	Calcite*	tr.
Pyroxenes	1	Siderite*	tr.
Apatite	tr.	Kaolinite**	5～20
Magnetite	tr.	Montmorillonite**	tr.～20
Allanite	tr.	Sericite**	tr.～ 5
Zircon	tr.	Chlorite**	tr.～ 3
Sphene	tr.	Limonite*	tr.～ 5
Ilmenite	tr.	Carbonaceous matter	tr.～ 1
Rutile	tr.	Uranium minerals	0.1～5
Epidotes	tr.		

* Found only in the oxidized ores.
** May be partly allogenic, or formed before the sedimentation.

Quartz in the deposits, is usually pale grey to greyish black in colour, which is due to the radioactivity of the ores. The depth of the colour is in proportion to the uranium content of the ore. The quartz crystals in the ores containing more than 0.15% U_3O_8 show invariably greyish black colour. They are often corroded to sub-rounded form, indicating the effect of the alkaline solution which seems to have prevailed in the deposits once. Potash-feldspars (microcline and orthoclase) and plagioclase are considerably altered into kaolinite and sericite. Biotite is found to be completely altered to chlorite or to vermiculite, while hornblende and pyroxenes are partly suffered from chloritization. Apatite can be found in the less uraniferous ores, but is hardly detected in the high grade ores. The other allogenic minerals are comparatively fresh. The alteration is generally stronger in the oxidized zone than in the unoxidized zone.

Uranium minerals

Three definite uranium minerals have been identified in the Ningyô-tôgé mine. They are ningyoite and uraninite in the unoxidized zone, and autunite in the oxidized zone. Humic acid or humate, biotite and limonite are found to be uraniferous in the deposits. Secondary uranium minerals other than autunite may occur in the mine, but not yet identified clearly, though some uranyl silicates, vanadates, and torbernite group minerals have been found in the Tôgô mine. Among these uranium minerals, ningyoite is probably most universally and abundantly distributed in the Ningyô-tôgé mine. It is principally a hydrated calcium uranous phosphate with various minor substituting ions, and the ideal chemical formaula is given as $Ca_{1-x}U_{1-x}R.E._{2x}(PO_4)_2 \cdot 1 \sim 2H_2O$. The mineralogical properties of the mineral was reported by the writer and his collaborators in details[20], and further study on the mineral especially concerning its genesis will be published in another paper.

Uraninite has been identified in the Yotsugi ore body[21], and also in the Nakatsugô, but not found in the Tôgé ore body even with carefull examination of the several uranium concentrates. The uraninite was so fine-grained that one could not observe individual grains under the microscope, and broadening of the X-ray diffraction lines took place. According to the results of the syntheses of uraninite (T. Muto's unpublished data), the broadness of the X-ray diffraction peak can be considered as the indication of the temperature of the formation—the lower the temperature of the formation, the broader the peak width, and hence it seems to have been precipitated at comparatively low temperature. The cell constant of the uraninite from the Yotsugi ore body was calculated to be $a_0 = 5.41 \pm 0.005$ Å. The mineral is intimately associated with ningyoite, and may have been precipitated contemporaneously with the latter.

Autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 10 \sim 12H_2O$, occurs coating surface of pebbles, filling their cracks, and cementing matrices of the conglomerate

in the oxidized zone. The mineral is variable in its appearence due to the variation of the chemical composition. Some contain abundant arsenic, and correspond to the intermediate phase between autunite and uranospinite, $Ca(UO_2)_2(AsO_4)_2 \cdot 10H_2O$. Autunite from the Ningyô-tôgé mine is characterized by containing considerable amount of strontium[13] which is apparently substituted for calcium. The autunite is generally found in the full-hydrate phase in drifts of the mine, but dehydrates into meta-I phase when left in a less humid atmosphere. The cell dimensions of the full-hydrate phase and the meta-I phase of the mineral are shown in Table 3.

Table 3. Cell dimensions of autunite and meta-autunite I.

		Ningyô-tôgé*	Synthetic[5]
Autunite	a_0	7.00±0.01Å.	7.003Å.
	c_0	20.72±0.02Å.	20.67 Å.
	$c:a$	2.960	2.952
Meta I	a_0	6.98±0.01Å.	6.99Å.
	c_0	8.45±0.01Å.	8.44Å.
	$c:a$	1.211	1.206

* Calculated with the Q-values, referring to J. Beintema's data[5].

Biotite was found to be radioactive by autoradiographic study of pebbles in the ore deposits. It was already shown by I. Hayase[10] that the radioactivity is appreciably concentrated in biotite crystals in the granite around the Ningyô-tôgé mine, but the radioactivity of the biotite in the ores is much stronger than that in the granite. This may be ascribed to the addition of uranium to the biotite from the ore solution.

Limonite occurs often associated with autunite in the oxidized zone of the deposits. Some limonite rich ores contain more than 0.1% U_3O_8, even though autunite is not detected in them. Autoradiographs of thin sections of the oxidized ores revealed that the limonite is always more or less radioactive. The mineral is submicroscopic in crystal size, and its X-ray powder pattern shows only weak lines of goethite, indicating mostly amorphous. T. G. Lovering[17] has described that uranium is fixed in limonite by adsorption. P. B. Barton Jr.[3] found that goethite of better crystallinity adsorbs less uranium than that of lower crystallinity. Thus, the adsorption of the ura-

nium which had been leached from ores by meteoric water, may have produced the uraniferous limonite.

Humic acid was found by the writer[21] very commonly in the conglomerate. It is always accompanied with ningyoite. The uranium content in the humic acid was found to be linearly related with the product of the organic carbon and the total uranium contents of the ore.

Authigenic minerals

The formation of the authigenic minerals are roughly classified into three stages. The first stage represents the diagenesis of the sediments, the second, the epigenesis, and the third, the recent oxidation by meteoric water. The first stage may represent the time of the deposition of the upper beds of the Ningyô-tôgé formation and possibly of the Takashimizu formation. Sulphide minerals and some clay minerals seem to have been formed in this stage. The second stage corresponds to the time of the uranium mineralization or the continuous period before and after it. Ningyôite, uraninite, gypsum, and sericite were formed probably in this stage. The typical sequence of these two stages is clearly shown in Fig. 2, Plate I. It indicates that the pyrite was formed after the sedimentation of the conglomerate and before the uranium mineralization. The third stage is represented by autunite, limonite, and carbonates in the oxidized zone. The limonite has been formed from iron sulphides and the calcite seems to have been fromed from carbonaceous matter, by oxidation, as they have not been detected in the unoxidized zone. It should be noticed, however, that calcite has been found with gypsum in the unoxidized zone of the Nakatsugô ore body and the Tôgô mine, where uraninite occurs together with ningyoite as the uranium minerals.

Sulphide minerals

Sulphide minerals found under the microscope are pyrite, marcasite and sphalerite, among which pyrite is exceedingly abundant than the others. The ores contain pyrite upto a few per cent, but usually less

than 1%. Marcasite is found rather frequently in some places, but not in other places. Marcasite occurs as minute crystal aggregate apart from pyrite, but in some cases occurs enclosed in pyrite. This may suggest that acidic condition prevailed in the conglomerate for a while just after the sedimentation, as marcasite has been considered to be formed at lower temperature in acid condition[22]. Sphalerite has been found in Drift No. 5 and Drift No. 2 of the Tôgé ore body, but generally it is hardly detected.

The pyrite from Drift No. 2 of the Tôgé ore body was separated by heavy liquid and floatation, and the separated sample was examined for the minor elements and with a decrepitation and heating microscope. It is low in cobalt and nickel contents (less than 10 ppm.)[8] and displays a curious decrepigraph without sign of the liquid inclusion. These data may indicate that it is not of common hydrothermal origin.

Gypsum

Fibrous gypsum is often found in drifts of the mine. Under the microscope, gypsum is classified into three types according to its occurrence. The first type is of the earliest formation and is coated or cut by ningyôite crystal aggregate as seen in Fig. 3-left, Plate I. The second type (Fig. 3-right, Plate I, Fig. 4, Plate II) seems to be of the same stage as the uranium mineralization. The third occurs filling cavities around ningyoite crystals, and it appears to have been precipitated later than ningyoite (Fig. 5, Plate II). All the gypsum occur in outside of pyrite mass, indicating its later precipitation.

Gypsum of type 1 forms always comparatively large crystals usually larger than 0.1 mm. It has clear cleavage traces in three directions perpendicular to each other. The cleavage pattern is the same as that of anhydrite, although the relief is much lower than the latter. This indicates that the gypsum is a pseudomorph after anhydrite, or that it has been converted from anhydrite which precipitated as the original mineral.

Gypsum of type 2 occurs generally replacing feldspar with seri-

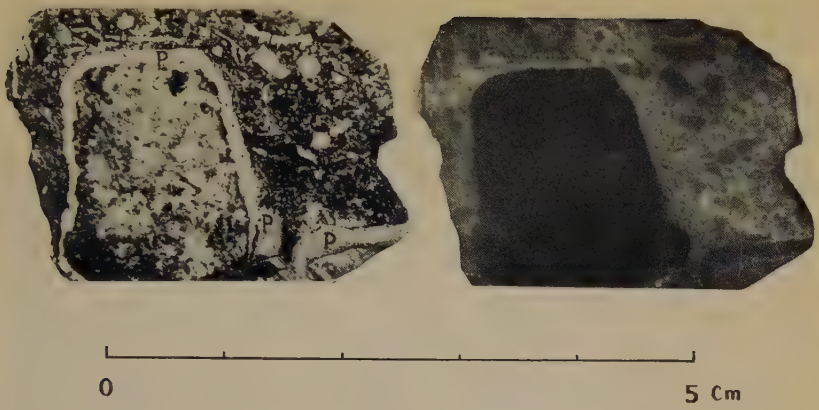

Fig. 2. Cross section of an unoxidized ore sample and its autoradiograph.

Left: photograph of the cross section.

Right: the autoradiograph.

The sample was taken from Drift No. 2-100 m, Tôgé ore body. Pyrite (P, white stripes in the left photograph) encloses pebbles or mineral grains, and is cut or enclosed by uranium minerals (bright part on the right photograph).

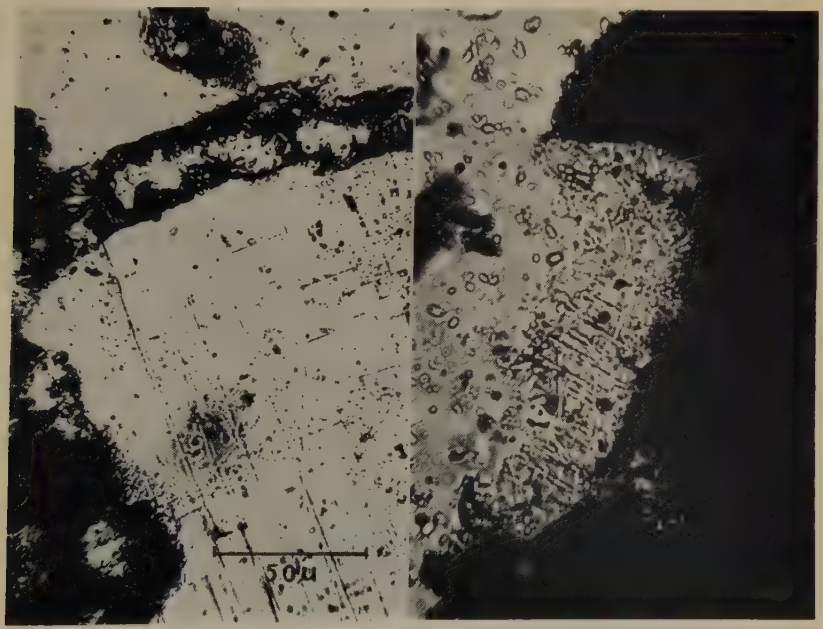

Fig. 3. Photomicrograph of gypsum and ningyoite.

Left: Ningyoite crystallizes on the surface and in the crack of the gypsum type 1, which has characteristic cleavage pattern of anhydrite.

Right: Gypsum type 2 coats pyrite(black mass) with tiny crystals of ningyoite (very fine particles near the pyrite mass). It looks like that of anhydrite origin.

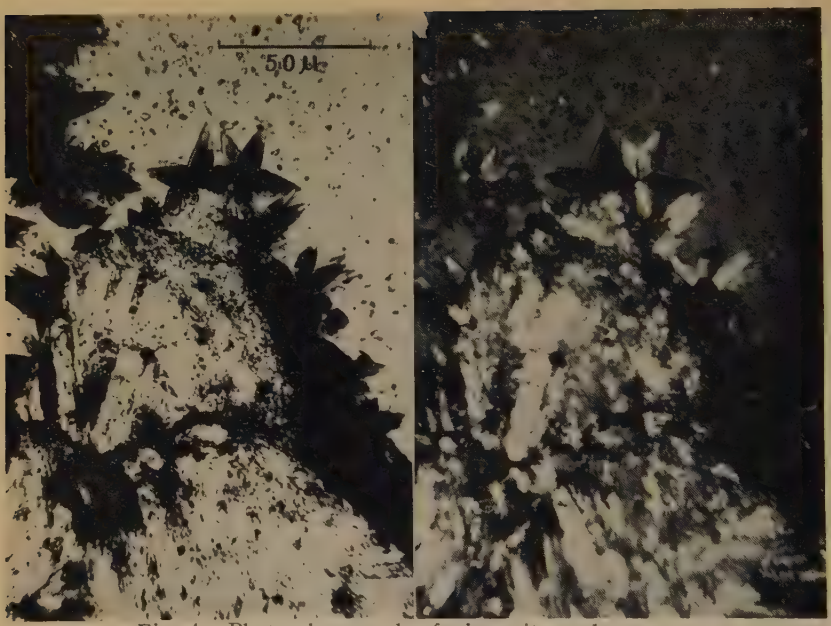

Fig. 4. Photomicrograph of ningyoite and gypsum replacing feldspar.
Feldspar is replaced by gypsum type 2 and sericite, and is coated by hexagonal petal-like crystals of ningyoite.
Left: Open nicol. Right: Crossed nicols.

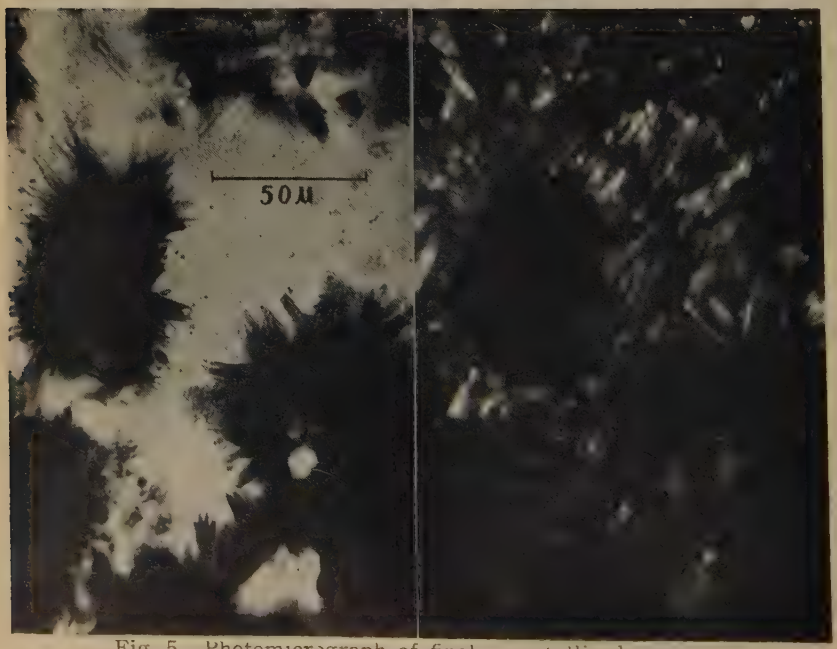

Fig. 5. Photomicrograph of finely crystallized gypsum filling a cavity around ningyoite.
Left: Open nicol. Right: Crossed nicols.

cite. Such replacement is found only in high grade ores where feldspar is coated by ningyoite crystals. It looks to have preceded before the precipitation of ningyoite in appearence, but may be considered to be simultaneous with the mineralization of ningyoite, because the coating of feldspar with tiny ningyoite crystals is not complete as seen in Fig. 4, Plate II. There are some gypsum crystals which look to belong to the third type outwardly as shown in Fig. 3-right. The crystals, however, are very intimately associated with extremely tiny crystals of ningyoite, and hence can be considered to be the contemporaneous precipitate with ningyoite or the second type, when carefully observed under the microscope. The gypsum is again presumed to be of anhydrite origin as seen in the photographs.

The third type is very fine grained acicular crystal, usually about ten microns in length, and was apparently precipitated as gypsum. However, the gypsum may have been partly reworked later by circulation of ground-water, as the solubilty of gypsum in cold water is considerably large (2.4 gr/*l*.). The gypsum of the third type is so fine in the crystal size that it may be a reworked product.

From those observations, it may be stated that the crystallization of calcium sulphate began before the uranium mineralization and after the precipitation of pyrite, and lasted still after the end of the uranium mineralization, mostly in the form of anhydrite.

Kaolinite and sericite

Kaolinite is the most abundant clay mineral in the mine. The crystal size is of order of tenth of micron, and the crystallinity is very poor as indicated in Fig. 6. The X-ray powder diffraction pattern of the kaolinite, which was obtained by an elutriation as a fraction less than one micron from an ore sample rich in kaolinite, coincides well with that of the poorly crystallized "Gaéromé" clay or the weathering product of granite. The kaolinite occurs extensively in both high and low grade ores, mostly replacing feldspar or filling cavities. The kaolinization of feldspar, however, is hardly observed around ningyoite crystals in the high grade ores, though

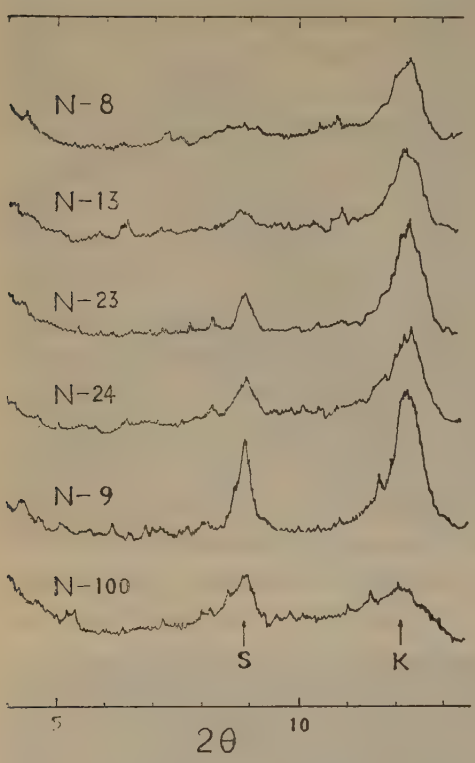

Fig. 6. X-ray diffraction charts of some ores at low 2θ angles.
S: sericite, K: kaolinite.
Cu$K\alpha$ radiation, 0.5°/min., full scale 500 cps., time constant 5 sec.

the feldspar enclosed in pyrite is kaolinized similary as in the low grade ores.

Sericite looks to have a pale green tint under the microscope, and the crystal size ranges from one to five microns. The mineralogical properties of the mineral is not clear as it was impossible to separate a pure sample. But, the elutriated sample shows clear independent X-ray diffraction lines at d=10.0, 4.98 and 1.639, indicating that the mineral is a kind of the potash-mica clay mineral, although the other lines are overlapped with those of kaolinite. Sericite occurs generally replacing feldspar spottedly with gypsum in the high grade ores, while it is found only sparsely in the feldspar enclosed in pyrite. Sericite occurs also intermixed with ningyoite in cavities of the high grade ores, but only small amount of the mineral is found in the low grade ores.

The above observation indicates that the kaolinization occurred before the sericitization which is apparently later than the precipitation of pyrite. The kaolinite may also have been formed before

the sedimentation of the conglomerate, but most of it probably was formed in the diagenic stage.

Distribution of some minerals and elements in the ore body

Uranium, some characteristic minerals and elements in ores of various grades from Ningyô-tôgé were determined quantitatively, and correlations between them were analyzed statistically.

Procedure

Twenty-four samples for analyses were collected from north-east running drifts across the major ore body of the Tôgé area. Besides, one sample from Drift No. 5 (D in Fig. 1) and two from a winze (C in Fig. 1) of the Tôgé ore body, and one from the Yotsugi ore body were added for comparison's sake. Most of the samples were taken from the basal conglomerate, except for a granite sample (N-42) and an andesite sample (N-41), both occurring along a fault (B in Fig. 1).

About 300 grams, excluding pebbles, of each conglomerate samples were collected at about one metre below the top of the conglomerate bed, except for N-106 and N-109. The collected samples were sieved in water and the fraction under one millimetre were left for 24 hours, decanted and dried at 90°C.

The samples thus obtained were chemically analyzed for P, S, As, Ca, Zn, Mo, Mn and U, as they have been very often detected in spectrographic analyses of the ores. The samples were decomposed by mixed acids of HCl, HNO_3 and H_2SO_4, except for the analyses of P, Ca and S. The P and Ca were analyzed after decomposing the samples by (1+1) HCl, to avoid analyzing the unnecessary portion of the elements which are contained in the allogenic minerals. Sulphur was taken into solution by mixed acids of HCl and HNO_3.

Quartz, kaolinite, montmorillonite, sericite and gypsum were analyzed quantitatively or semi-quantitatively with X-ray diffractometer. A direct method was applied for the analysis measuring the mass-absorption coefficient. The fundamental equation for the method was given by J. Leroux and others[16] as follows:

$$X_i = \frac{I_i \cdot \mu_s^*}{(I_i)_0 \cdot \mu_1^*}$$

where, X_i is content of the i'th component of the sample analyzed, I_i and $(I_i)_0$ are the intensities of the X-ray diffracted by some selected plane of the i'th component of the sample and of the standard sample of the i'th component, respectively, and μ_s^* and μ_1^* are the mass absorption coefficients of the sample and the standard sample, respectively. Some artificially mixed samples of quartz and other minerals in various ratios were analyzed for testing the validity of the above equation, and fairly good results (relative errors less than 5%) were obtained. The details of the method will be published in future.

The standard minerals were selected to be similar in crystallinity to the minerals contained in the ores as far as possible, because it affects the accuracy of the analyses in the case of the clay minerals. They are kaolinite from Gifu Prefecture (so-called Hara Gaéromé clay), montmorillonite from the Tôgô mine, Tottori Prefecture, and sericite from the Inamé mine, Aichi Prefecture. All the samples were filled and X-rayed in a normal glass sample holder, and preferentially orientated slides were also used for the analyses of montmorillonite and sericite, as their contents in the samples were generally low.

Results

The results of both mineralogical and chemical analyses of the ores are shown in Table 4, where clay mineral in parentheses such as (Kt) means the percentage of the clay mineral in the total clay minerals, given by dividing the content of each clay mineral by the sum of content of kaolinite, montmorillonite and sericite in a sample. The values thus obtained should represent more adequately the true variation of the content of each clay mineral in a series of the ore samples, while, in such a small amount of the sample, the total clay content might be affected by the uneven distribution of constituent materials of the conglomerate.

The arithmetic mean of the uranium contents is found to be much

larger than the abundance in the earth's crust, while those of the other elements are not so different from the abundances except for calcium and manganese, which should have been less detected than the true contents, as the rock-forming minerals containing them were not decomposed, and only the portion contained in the acid soluble minerals (mostly authigenic) were analyzed. The coefficient of variation is given by dividing standard deviation by arithmetic mean, and indicates the degree of variation of the content from place to place. Therefore, the elements and the minerals which have been deposited syngenetically with the sediments, should give smaller values of the coefficient, as in the case of quartz in Table 4. On the other hand, epigenetically formed or precipitated minerals and elements must have larger values. The coefficient, thus, can be considered as the indication of the degree of the epigenesis for each element and mineral. Most of the values are comparatively high except for those of Ca, Mn, kaolinite and quartz. The values for cpm., U_3O_8, Zn and montmorillonite are so high that they may probably be of epigenetic origin.

The significance of the analyzed values of elements and minerals, or the relations among them are better understood by statistical treatment. In order to know the correlations among them, rank correlation method, which has been introduced to geochemists by F. J. Flanagan[7] was applyed. The coefficient is calculated as follows. In a set of n samples, the data are arranged in increasing numerical value for each element, and then are numbered according to their rank from 1 to n. Then, the rank correlation coefficient ρ is obtained by formula:

$$\rho=1-\frac{6\Sigma D^2}{n(n^2-1)}$$

where, D is the difference of the two ranks given for each sample.

The rank correlation coefficients were calculated for 24 samples excluding samples, N-72, N-41 and N-42, because these were different from the other samples in locality or in rock species. It is known

Table 4. Analyses of the uranium ores for some minerals and elements.

Sample	Locality[3]	Rad. (cpm)	U_3O_8 (%)	P (%)	S (%)	As (ppm)	Ca (%)	Zn (ppm)	Mo (ppm)	Mn (%)	Qz[6] (%)	Gm[6] *	Kt[6] (%)	St[6] (%)	Mt[6] (%)	(Kt) (%)[7]	(St) (%)[7]	(Mt) (%)[7]
N-3	T 2-130-S81	9	.03	.012	.11	<2.5	.10	40	4	.013	42	+	11.9	.6	.1	95	5	<1
N-4	Do 75. 5	11	.04	.015	.04	<2.5	.08	40	<4	.025	38	+	8.9	.5	.1	94	5	1
N-6[1]	Do 65	21	.04	.021	.05	<2.5	.12	40	<4	.014	37	+	12.5	.8	.1	94	6	<1
N 8	Do 55	24	.04	.017	.07	5.0	.08	40	20	.010	46	2+	6.1	.3	.1	94	5	1
N-9	Do 50	508	.23	.117	.15	12.5	.28	40	<4	.007	66	4+	11.3	1.3	.1	89	10	1
N-11	Do 40	116	.08	.037	.10	2.5	.13	20	<4	.008	42	2+	5.9	.4	.2	91	6	3
N-13	Do 35	16	.04	.014	.04	<2.5	.09	20	<4	.008	47	+	5.4	.2	.2	94	3	3
N-14	Do 20	39	.06	.034	.09	7.5	.14	20	4	.007	44	3+	7.4	.6	.5	87	7	6
N-16	Do 10	625	.28	.078	.04	5.0	.17	20	<4	.004	42	3+	5.3	.8	.4	82	12	6
N-18	Do 0	811	.39	.132	.31	2.5	.19	160	<4	.014	46	3+	5.1	1.1	.1	82	17	1
N-19[1]	T 2-125	25	.05	.033	.09	7.5	.19	40	4	.011	24	+	21.3	.2	.5	97	1	2
N-21	T 2-110-N 5	27	.05	.031	.07	<2.5	.27	40	<4	.015	47	4+	9.7	.5	.6	89	5	6
N 23	Do 15	77	.08	.047	.08	<2.5	.12	20	<4	.014	46	+	9.4	1.3	.7	83	11	6
N-24[1]	Do 20	183	.06	.031	.11	<2.5	.13	20	<4	.007	46	+	6.5	.8	.4	85	10	5
N-26	Do 30	63	.11	.045	.23	<2.5	.38	64	<4	.007	40	5+	8.3	.5	.2	92	6	2
N 29	Do 45	59	.09	.048	.18	12.5	.14	40	12	.010	49	3+	6.5	.6	.1	91	8	1
N-32	Do 60	56	.07	.048	.31	10.0	.40	20	12	.011	35	4+	5.9	.3	.6	87	4	9
N-33[1]	Do 65	103	.06	.036	.09	<2.5	.09	20	8	.015	32	+	3.9	.3	.4	84	7	9
N-36	Do 80	458	.17	.088	.33	<2.5	.26	20	16	.017	34	2+	5.7	.5	1.1	78	7	15
N-38[2]	Do 90	1266	.88	.093	.16	15.0	.22	140	12	.022	21	5+	2.6	.4	1.2	61	10	29
N-40[1]	Do 95	243	.09	.039	.25	<2.5	.28	40	8	.011	32	2+	3.0	.8	1.6	67	15	18
N 41[1]	Do 95. 7	24	.04	.049	.04	2.5	.11	140	20	.031	0	+	3.4	.4	6.0	35	4	61
N-42	Do 96. 5	7	.06	.062	.04	<2.5	.32	72	20	.028	19	+	9.8	.4	3.4	72	3	25
N-72[1]	Y 1-310-S25	748	.56	.082	.04	2.5	.14	140	<4	.009	34	2+	8.8	1.0	.9	83	9	8
N-100	T 5-290	660	.32	.084	.32	<2.5	.07	260	<4	.004	31	4+	4.4	1.3	.1	77	22	1
N 106	T 2-90-W-low	345	.40	.051	.14	2.5	.14	40	<4	.025	55	2+	8.7	1.3	.9	80	12	8
N-109	Do..... up	238	.34	.039	.07	2.5	.15	64	<4	.021	33	2+	6.5	.8	1.3	76	9	15

Mean ($\bar{x}$)	250	.17	.051	.13	3.9	.18	60	7	.014	38	.9	7.6	.7	.8	83	8	9	
Coefficient of variation ($\sigma/\bar{x}$)	1.27	1.14	.60	.73	1.03	.51	.95	.77	.53	.33	.76	.50	.52	1.53	.15	.57	1.40	
Mean abundance in the earth's crust[4]		.0004[5]	.118	.052	5	3.63	132	15	.10									

Analyst: T. Ashizawa, Atomic Fuel Research Laboratory, for the elements.
T. Muto for the minerals.

[1] Sample oxidized a little, and stained by limonite.

[3] Sample oxidized completely, and colored to dark brown.

[2] Localities should be read as following examples:
T2 110-N15 is a point at *15 m.* apart from the junction of Drift No. *2-110* m. *N*orth extention of the *T*ôgé ore body. Y1-310-S25 is a point at *25* m. apart from the junction of Drift No. *1-310* m. South extention of the *Y*otsugi ore body. T2-90-W-low is a point at the *low*er part of the *w*inze at Drift No. *2-90* m. of the *T*ôgé ore body.
N-41 is a sample of andesite dyke intruded along a fault. N-42 is a sample of the base granite at the point 50 cm. apart from the fault. The other samples are all from the basal conglomerate.

[4] Cited from B. Mason's "Principles of Geochemistry", John Wiley & Sons, New York, (1952).

[5] Abundance of U, and not of U_3O_8.

[6] Abbreviation of the minerals:
Qz: quartz, Gm: gypsum, Kt: kaolinite, St: sericite, Mt: montmorillonite.

[7] Clay mineral in parentheses such as (Kt) denotes the percentage of the clay mineral in the total clay minerals, given by dividing the content of each clay mineral by the sum of the three clay minerals.

* Gypsum content should be estimated as follows:
$+<0.5\%<2+<1.0\%<3+<1.5\%<4+<2.0\%<5+<3.0\%$.

Table 5. Rank correlation coefficients between some minerals and elements in the uranium ores.

	U	P	S	As	Ca	Zn	Mo	Mn	Qz	Gm	Kt	St	Mt	(Kt)	(St)	(Mt)
cpm	+.92	+.88	+.54	+.31	+.27	+.29	+.03	−.05	−.14	+.51	−.57	+.50	+.37	−.84	+.83	+.43
U		+.91	+.58	+.40	+.44	+.42	+.01	+.06	−.09	+.61	−.44	+.50	+.42	−.79	+.76	+.43
	P		+.65	+.44	+.50	+.30	+.13	−.03	−.05	+.65	−.40	+.45	+.28	−.68	+.69	+.31
		S		+.13	+.45	+.33	+.41	−.08	−.21	+.51	−.34	+.21	+.15	−.42	+.39	+.16
			As		+.40	+.21	+.46	−.05	+.16	+.52	+.02	−.02	+.15	+.02	+.10	+.15
				Ca		+.16	+.23	+.02	−.04	+.60	−.10	+.02	+.50	−.26	+.08	+.45
					Zn		+.15	+.24	−.12	+.42	−.08	+.32	−.09	−.07	+.31	−.18
						Mo		+.29	−.18	+.12	−.16	−.33	+.29	+.07	−.10	+.35
							Mn		−.17	−.21	+.09	−.07	+.36	−.18	−.07	+.34
									Qz	+.05	+.33	+.30	−.27	+.31	+.04	−.31
										Gm	−.24	+.16	+.16	−.32	+.30	+.20
											Kt	+.13	−.24	+.64		
												St	−.03		+.81	
													Mt			+.95
														(Kt)	−.78	−.69
															(St)	+.23

The abbreviation of the minerals is given in Table 4.

The rank correlation coefficients in this table were calculated from the values in Table 4, with 24 samples excluding samples, N-41, N-42 and N-72.

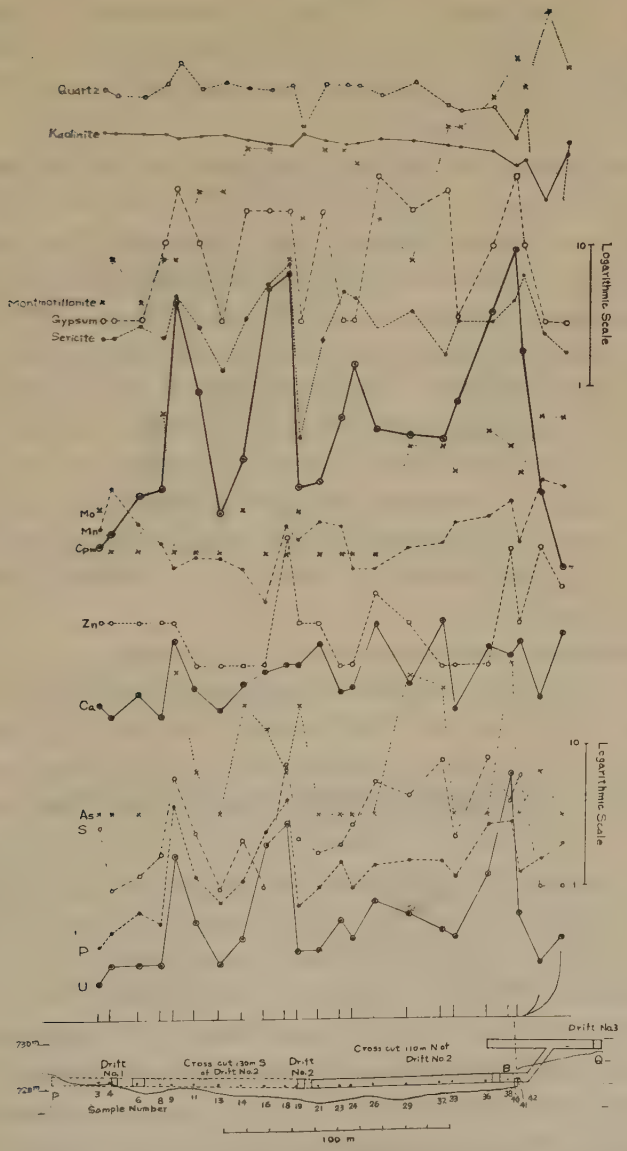

Fig. 7. Distribution of some minerals and elements in the Tôgé ore body.
Abundances in logarithmic scale.

from the critical values of ΣD^2 that the correlation is significant for probability 0.05 or for 95% confidence, if the absolute value of ρ is not less than 0.40, and significant for probability 0.01 or for 99% confidence, if not less than 0.52[7].

The correlation coefficients thus calculated for each pair in Table 4 are given in Table 5. It is indicated in the Table that most of the coefficients are positive except for pairs concerned with kaolinite, quartz and Mn. This seems to indicate that these minerals and element were mostly deposited during the deposition of the conglomerate, and thus tended to assemble in the trough carved on the base granite as shown in Fig. 7. Pairs with positive correlation for probability 0.01 excluding those with cpm. are found to be U-P, U-S, U-gypsum, U-(sericite), P-S, P-gypsum, P-(sericite) and Ca-gypsum, while the negative correlation for the same probability are U-(kaolinite), P-(kaolinite), (kaolinite)-(sericite) and (kaolinite)-(montmorillonite). These may suggest the presence of genetically important relation between each pair.

Correlation between uranium and constituent minerals

The correlation of uranium with kaolinite or with sericite is very good as indicated in the high absolute value of the correlation coefficients. The correlation was found to be roughly linear with logarithm of U_3O_8 percentage rather than with percentage itself as shown in Fig. 8. The positive correlation of uranium with sericite and the negative correlation with kaolinite are more decidedly illustrated in the correlation diagram between the uranium content and the sericite to kaolinite ratio (Fig. 9), whose coefficient is calculated to be +0.86. The coefficient is higher, when cpm. is used instead of U_3O_8 content, and reaches to +0.89. The better correlation with cpm. than with U_3O_8 is probably caused by the recent differential leaching of uranium from its daughter products. In Fig. 9 all the spots are distributed linearly except for one numbered 100. The N-100 sample is so rich in uranium adsorbed in humic acid that the uranium might have been partly dissolved in water when the sample was decanted.

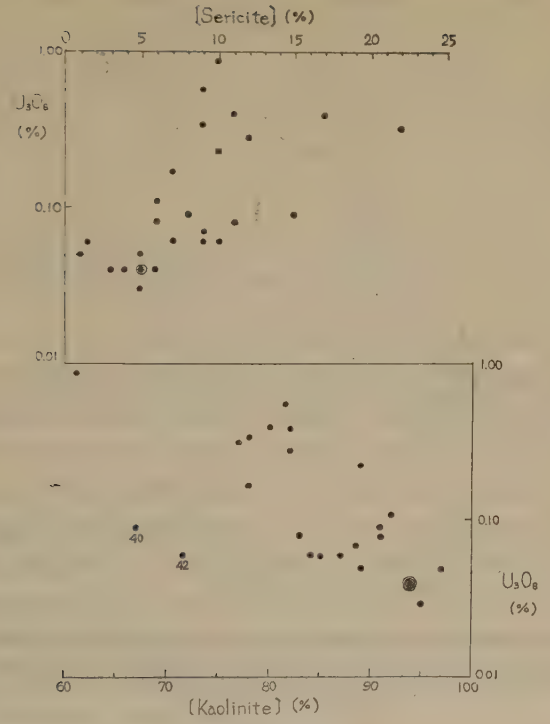

Fig. 8. Semi-logarithmic diagram showing correlation of uranium with sericite and kaolinite in the Ningyô-Tôgé ores. U_3O_8 in logarithmic scale.

The equation between logarithm of U_3O_8 percentage and sericite to kaolinite ratio was calculated by the least square method as follows:

$$\text{sericite/kaolinite} = 9.9 \log U_3O_8 + 19.7 \quad (\text{for } U_3O_8 \text{ from } 0.04 \text{ to } 0.9\%)$$

This relation can be accounted for only by the assumption that kaolinite was transformed into sericite by the uranium containing ore solution. Because, (1) the correlation of kaolinite or of sericite is not so good with the other elements as with uranium, (2) kaolinite is of poor crystallinity and supposed to be a weathered product, and (3) microscopic observation indicates that feldspar is mostly

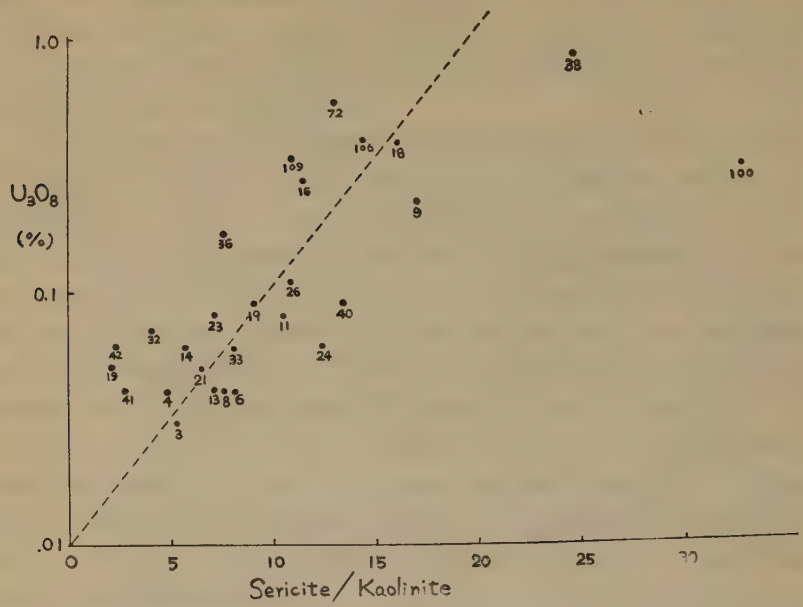

Fig. 9. Semi-logarithmic diagram showing correlation between uranium content and sericite to kaolinite ratio in the Ningyô-Tôgé ores. U_3O_8 in logarithmic scale.

replaced by sericite and gypsum around nigyoite, while it is mostly kaolinized when enclosed completely in pyrite or in low grade ores.

Sericite or illite has been found in some of the sandstone type uranium deposits[2) 9)], but its clear correlation with uranium has not been reported yet. T. F. Bates and E. O. Strahl[4)], on the other hand, recognized a negative correlation of uranium with illite content, in uranium-bearing black shales. The discrepancy of the both cases seems to be explained by the different mechanism of the uranium concentration.

Montmorillonite appears to have a positive correlation with uranium for 0.05 probability, but it is doubtful whether it is truely related to uranium or not. Their association can not be observed from Drift No. 1 to Drift No. 2 as shown in Fig. 7, and hence the

Table 6. Effect of assortment of the pebbles in the conglomerate on the montmorillonite to kaolinite ratio.

Granite pebbles*	Number of sample	Montmorillonite to kaolinite ratio	Standard deviation
>70%	11	2.6%	2.6%
70~30	9	7.4	5.2
<30	4	21.5	14.8

* Determined for the pebbles from 2 to 20 mm. in their sizes. Other pebbles are mostly of andesitic rocks.

correlation may be accidental. The montmorillonite content of the ore was found to be mostly affected by the constituting materials of the conglomerate in each place. Table 6 shows the relation between the kaolinite to montmorillonite ratio and the kind of pebbles. It is apparent from the Table that montmorillonite content increases with increasing andesitic pebbles in the conglomerate. The same thing is recognized also from the correlation coefficients of pairs among quartz, montmorillonite and kaolinite. The coefficient of quartz with montmorillonite shows a negative value, while that with kaolinite has a positive value, and the coefficient between both clay minerals is definitely negative.

Montmorillonite is a very predominant mineral in the ores of the Tôgô mine where the country rocks are mostly tuff breccia. Some white ore is almost entirely composed of pure montmorillonite. T. Sudo (oral communication, 1960) mentioned that there may be a negative correlation between uranium and montmorillonite contents of the ores of this type.

Gypsum has a comparatively high correlation coefficient with uranium, though it has similarly high coefficient with P and Ca. The good correlation of gypsum with uranium may indicate together with the above mentioned microscopic observation that most of the gypsums present in the ores have been precipitated simultaneously with uranium, though the gypsum had a longer period of precipitation than the uranium. The association of gypsum with uranium minerals in

the sandstone type deposits is not common, and instead calcite is very often associated with uranium. The fact is very important in relation with the properties of the ore solution.

Pyrite has not been analyzed quantitatively, but the microscopic observation indicates that uranium is always associated more or less with pyrite in the unoxidized zone. H. Araki and K. Kubo[1] found that the content of iron sulphide, which was determined chemically, increases with increasing uranium. The good correlation, however, may be applied only in each localized area, and may become poor when it is considered throughout the wide area of the deposits. Because, in some places of the deposits where pyrite is very rich, the ores contain comparatively small amount of uranium, while some of high grade ores have only trace of pyrite. It is very common phenomenon in all kinds of uranium deposits that uranium is intimately associated with pyrite and other sulphides. The sulphides have been considered to act against uranium as reducing agent by sulphide ion or ferrous ion contained in them, and to cause the precipitation of uranium. Hence, the association of uranium and pyrite in the deposits may be regarded as the result of those mechanism of deposition, but not to indicate more intimate relation between them.

Correlation between elements

A very good correlation between uranium and phosphorus in the unoxidized zone of the Tôgé ore body has been shown by M. Sakanoue[23] in the samples which were taken vertically from the top to the bottom of the conglomerate at a few spots. The samples of this study which were collected horizontally for comparatively long distance also show higher correlation coefficient between them than all other pairs of elements in Table 5. Analytical values of U_3O_8 and P are plotted in Fig. 10, where the former values are again in logarithmic scale, as it shows better linearity with P. The ores of higher grade were found to have similar U/P ratio as that of ningyoite[20], but in the lower grade ores, phosphorus is contained much more than expected from the ratio. This may indicate that most of the uranium

contained in the unoxidized ores exists as ningyoite, and the other phosphate minerals such as apatite occurs only in the lower grade ores. The uranium-phosphorus correlation is also demonstrated in the phosphatic beds very commonly[18], but the correlation is not so good as in the Ningyô-tôgé deposits. The correlation coefficient was reported to be +0.68 for the phosphate district of Florida, U. S. A.[6].

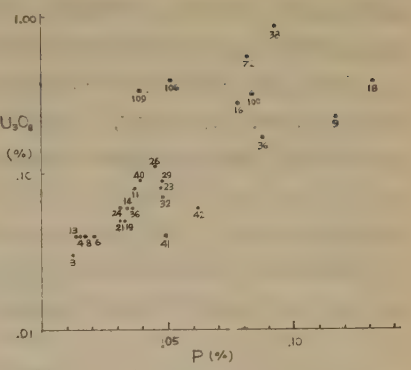

Fig. 10. Semi-logarithmic diagram showing correlation between uranium and phosphorus in the Ningyô-tôgé ores.

The correlation coefficient between uranium and sulphur is also remarkable attaining +0.58. The high coefficient is due to the fact that most of the sulphur is contained in gypsum and pyrite, which are intimately associated with ningyoite.

Acid-soluble calcium has also significant correlation coefficient with uranium. This seems to be caused by the fact that most of the calcium is contained in gypsum. Some of the calcium, however, should be contained in montmorillonite, as the coefficient between them is as high as +0.50.

Arsenic and zinc are also correlated with significant positive coefficient. The former seems to be contained mostly in pyrite or its altered products, as the arsenic content of pyrite is very high (0.71 and 0.76% As[23]), and the latter exists mostly as sphalerite which is presumed to have been precipitated syngenetically with at least a part of pyrite.

Molybdenum has no correlation with uranium, but has with sulphur and arsenic. It is often associated with uranium in some of the sandstone type uranium deposits[14].

Manganese has no correlation with uranium nor with other ele-

ments and minerals, though comparatively good correlation with montmorillonite and with molybdenum are indicated in Table 5.

X-ray spectrographic analyses were made for the samples from N-3 to N-18. U, Fe, Sr, Y, Ba, Zr, Cu, Pb, Zn, Mn, Cr, Mo and Sn have been detected in most of them. However, among these elements, only yttrium and strontium were found to increase with increasing uranium content. The good correlation between uranium and yttrium or strontium has been already reported by N. Katayama and H. Takeda[13] on vertically collected samples in the Tôgé ore body.

Conclusion

In conclusion the authigenic minerals of the Ningyô-tôgé uranium ores can be classified into three stages from the paragenetic point of view. The first stage corresponds to the diagenesis of the country rock, and at this stage kaolinization of feldspar, precipitation of pyrite and marcasite, a part of montmorillonitization occurred. The second stage is that of the uranium mineralization or the continuous period before and after it. Ningyoite, uraninite and gypsum were precipitated at this stage from the extrinsic ore solution which transformed kaolinite into sericite. The third stage represents the oxidation by the recent meteoric water, and autunite, limonite and carbonate minerals were formed in the oxidized zone.

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THE CRYSTAL STRUCTURE OF ANTLERITE

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Abstract

The crystal structure of antlerite has been worked out by means of the heavy atom method through the two-dimensional Patterson and Fourier syntheses. The lattice constants of the mineral are $a_0=8.23\pm0.02$Å., $b_0=12.00\pm0.02$Å. and $c_0=6.03\pm0.01$Å. Its space group is Pnam, and there are four chemical units of composition $Cu_3(SO_4)(OH)_4$.

The structure is composed of chains of octahedra formed by oxygen atoms and hydroxyl groups linked with copper atoms, and there are two types of non-equivalent copper atoms having different coordination.

Introduction

In the present study, the crystal structure of antlerite was determined as a part of investigation of the basic copper sulphate minerals to find some structural characteristics as compared with other members of basic copper minerals.

Only one report of X-ray study on antlerite has been published by Richmond[5] giving the lattice constants, space group and the unit cell contents.

Experimental

For this study, specimens from Chuquicamata, Chile, were used. They were prismatic in shape elongated along the c-axis. The lattice constants were determined with the rotation photographs about the three principal axes as follows:

$a_0=8.23\pm0.02$Å., $b_0=12.00\pm0.02$Å., $c_0=6.03\pm0.01$Å.

There are four chemical units of composition $Cu_3(SO_4)(OH)_4$. Systematically absent reflections were $(0kl)$ for $k+l$ odd, $(h0l)$ for h

odd, and (h00), (0k0) and (00l) for odd indices, and the crystal showed morphologically holohedral symmetry. Accordingly, the space group of the mineral was indicated to be Pnam. These results are in good agreement with those previously reported.

Intensity data were collected from zero layer integrating Weissenberg photographs about the three principal axes with Ni-filtered Cu$K\alpha$ radiation (λ=1.5405Å.). All relative intensities were estimated visually and corrected for the Lorentz and polarization factors as usual. No corrections for variation in intensities due to absorption, temperature factors and extinctions were made, but absorption due to the shape effect was minimized with comparison between the equivalent reflections in the intensity estimation. These corrected intensities were converted to the absolute scale applying Wilson's method for the observed structure factors.

Throughout the stages of calculation, atomic scattering curves for the neutral atoms were used; that for oxygen was taken from the values given by Berghuis et al[5], sulphur from those by Tomiie and Stam[7], and copper from those by Thomas and Umeda[6]. The contribution of hydrogen atoms to the structure factors was excluded from calculation in any case.

Structure analysis

As the first step of the determination of atomic coordinates, two-dimensional Patterson synthesis $P(UV)$ and complementarily sharpened Patterson synthesis $P_s(UV)$ were carried out using observed hk0 structure factors. As shown in Fig. 1, five prominent peaks with nearly equal height were found besides the one at the origin, and assumed to represent the symmetrical and asymmetrical copper-copper vector peaks which were equally weighted. From the positions of these peaks, approximate x- and y- coordinates of copper atoms were easily obtained, and further, from the inspection of 00l reflections, it was directly discovered that the way to allot twelve copper atoms to the equivalent positions was restricted to the following; 4(c) with

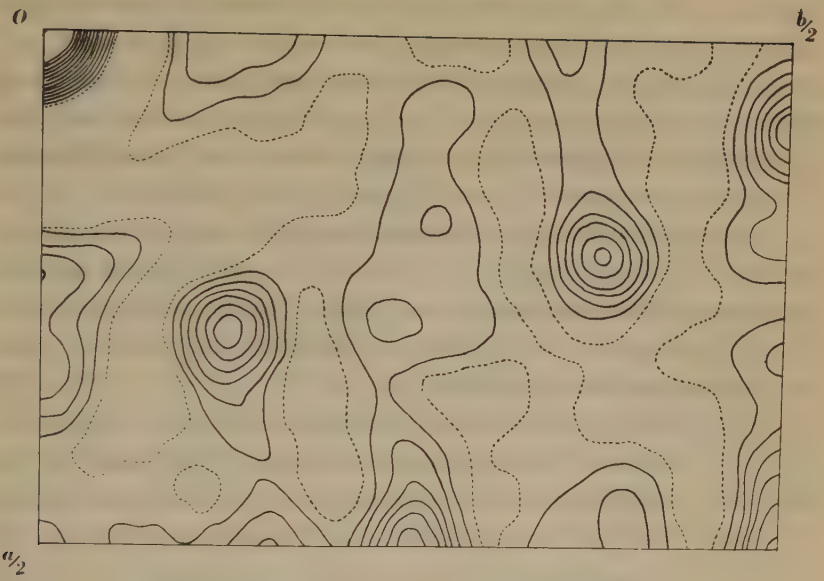

Fig. 1. The Patterson projection on the (001) plane.
Contours at an arbitrary unit.

x=0.00 and y=0.00, and 8(d) with x=0.29 and y=0.125. This consequence was also conformable to the interpretation of $P(VW)$ as well as $P(UW)$.

After the establishment of x- and y- coordinates of copper atoms, $hk0$ structure factors based on the copper contributions only were calculated, and compared with the observed ones. Then the signs of twenty five reflections having large absolute values were determined exactly. On the basis of this sign determination, still taking the copper contribution into account, sign relationship, $S(h)=S(S(h')S(h+h'))$, was additively employed for the sign determination of the reflections having relatively low U-values. And the signs of additional sixty four reflections were determined.

Subsequently, Fourier projection, $\rho(xy)$, was prepared using, as coefficients, those observed structure factors, whose signs were reasonably fixed. From height ratios and positions of Fourier peaks, a

number of maxima were distinguished, viz. copper, sulphur, oxygen atoms and hydroxyl groups of 8(d). Furthermore four peaks of light atoms were found. They are more or less distorted and diffuse, their positions being necessarily 4(c). It was also expected that locations of atoms in the foregoing were rather suitable from a consideration of a spatial arrangement keeping atoms in their positions.

Hereon, $hk0$ structure factors were computed based on the coordinates for the selected peaks, and then Fourier projection, $\rho(xy)$, was synthesized. This procedure was repeated, giving necessary shifts in the atomic positions, in order to increase terms settled in sign and to decrease reliability factor.

As another approach to the problem, to exclude the effect of diffraction ripples for refining the coordinates of the light atoms, difference synthesis, $\rho_d(xy)$, was carried out with coefficients in which the copper and sulphur contributions were subtracted from the ob-

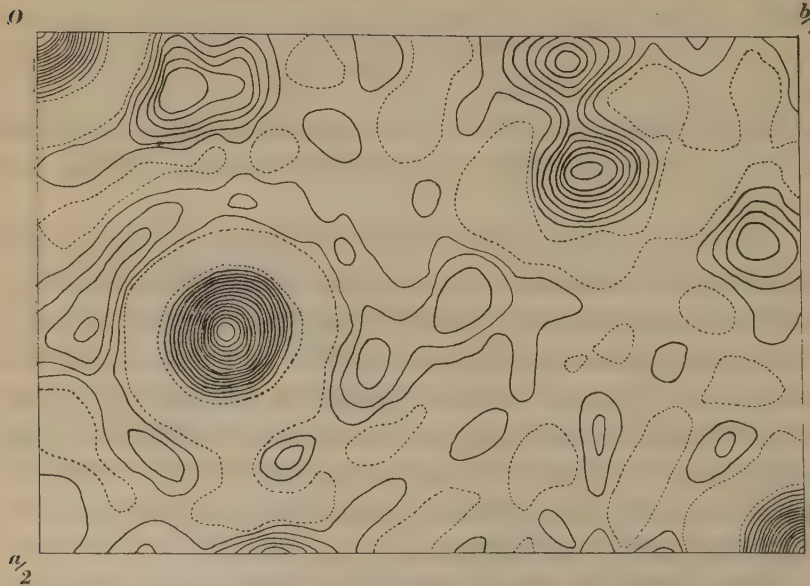

Fig. 2. The final F_o synthesis projected on the (001) plane. Contours are drawn at intervals of 10e A^{-2} for copper and those for other atoms at intervals of 5 e$Å^{-2}$. Zero contours dotted.

served structure factors.

The settlement of the x- and y-coordinates necessarily permitted that tentative positions for z-coordinates of 8(d) could be readily taken in a limited range. Therefore, both $0kl$ and $h0l$ structure factors were calculated and Fourier projections were prepared in the same way as done for $\rho(xy)$ and $\rho_d(xy)$.

These syntheses were performed with the 1/120 Beevers and Lipson's strips.

In the initial stages on the Fourier projections, positions of atoms were obtained, for the resolved peaks with an application of the Gaussian curve, and for the partly overlapping atoms with a standard peak form. In the final stages, the coordinates of atoms were revised with successive difference syntheses, $\rho_o - \rho_c$.

In Figs. 2 and 3 are shown the Fourier projection of electron

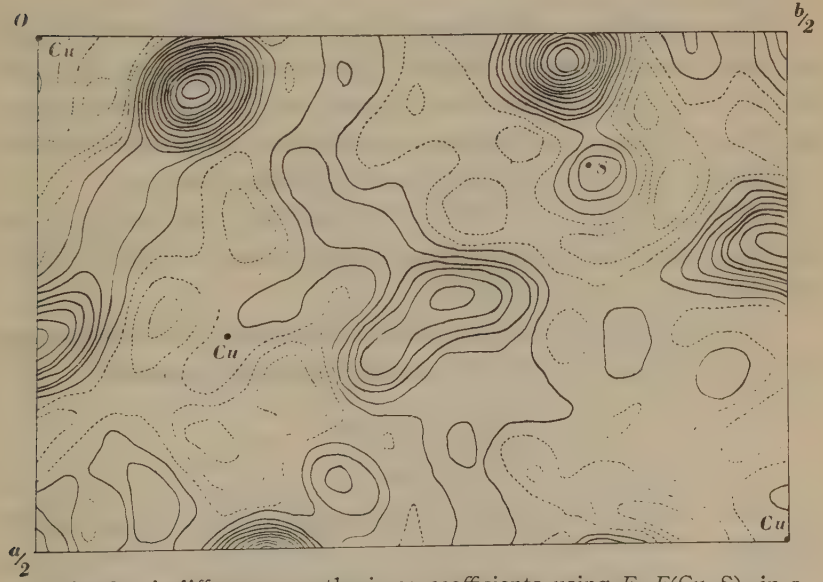

Fig. 3. A difference synthesis as coefficients using F_o-F(Cu, S), in a stage close to the final one. Contours are drawn at intervals of 2.5 eA^{-2}, zero and negative contours dotted. Positions of copper and sulphur atoms are marked by solid circles.

Table 1. Coordinates of atoms.

Atom	Number of atoms in a unit cell	x	y	z
Cu (1)	4	0.004	0.002	0.250
Cu (2)	8	0.290	0.125	0.005
S	4	0.130	0.362	0.250
O (1)	4	0.258	0.273	0.250
O (2)	4	0.203	0.475	0.250
O (3)	8	0.025	0.346	0.046
OH (1)	4	0.283	0.017	0.250
OH (2)	4	0.685	0.775	0.250
OH (3)	8	0.053	0.104	0.516

density along [001], obtained in the final stages.

The coordinates of atoms found in the final synthesis are given in Table 1.

The comparison of the observed and calculated structure factors are presented in Table 2, in which the calculated values were computed with the atomic coordinates finally obtained and the observed ones were readjusted with factors that minimize the reliability factors. No attempt was made for evaluating temperature factors.

The reliability factors are 13.4, 14.3 and 16.1% for $hk0$, $0kl$ and $h0l$ reflections respectively, missing reflections due to weak intensity being included in the calculation.

As an estimation for errors, standard deviations of the coordinates for the resolved peaks were estimated, using the expression

$$\frac{\frac{2\pi}{A}\cdot\frac{1}{a}\{\Sigma\Sigma h^2\Delta F^2\}^{\frac{1}{2}}}{2P\rho_{\max}}$$

in which A is the area of the projection and P, a function of atomic shape.

They are 0.003 and 0.0022Å. for copper, 0.011 and 0.017Å. for sulphur, and 0.016 and 0.020Å. for oxygen atoms and hydroxyl groups, for $\sigma(x)$ and $\sigma(y)$ respectively.

Table 2. Observed and calculated structure factors.

h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	0		684	2, 10,		0	67	55
2	0	0	68	− 79	2, 12,		0	155	164
4	0	0	221	213	2, 14,		0	70	39
6	0	0	66	66	2	1	0	10	15
8	0	0	22	16	2	3	0	17	− 14
10,	0	0	90	109	2	5	0	14	4
0	2	0	77	95	2	7	0	37	− 37
0	4	0	113	−136	2	9	0	—	12
0	6	0	112	110	2, 11,		0	40	38
0	8	0	252	284	2, 13,		0	18	− 21
0	10,	0	47	43	2, 15,		0	31	− 39
0	12,	0	72	− 66	3	1	0	165	231
0	14,	0	76	71	3	3	0	27	21
0	0	2	44	37	3	5	0	<14	− 2
0	0	4	299	347	3	7	0	167	140
0	0	6	—	− 1	3	9	0	174	163
1	1	0	39	40	3, 11,		0	<22	− 15
1	3	0	145	188	3, 13,		0	9	− 10
1	5	0	74	68	3	2	0	110	135
1	7	0	21	− 8	3	4	0	39	− 30
1	9	0	78	76	3	6	0	134	−124
1,	11,	0	121	121	3	8	0	66	50
1,	13,	0	38	35	3, 10,		0	110	86
1,	15,	0	—	10	3, 12,		0	40	− 29
1	2	0	153	−172	3, 14,		0	72	− 77
1	4	0	30	− 20	4	2	0	76	80
1	6	0	113	141	4	4	0	37	30
1	8	0	32	29	4	6	0	87	71
1,	10,	0	95	−106	4	8	0	123	121
1,	12,	0	22	− 28	4, 10,		0	75	68
1.	14,	0	74	87	4, 12,		0	18	18
2	2	0	81	88	4, 14,		0	29	28
2	4	0	112	113	4	1	0	131	−157
2	6	0	83	83	4	3	0	107	−106
2	8	0	57	− 61	4	5	0	114	95

Table 2. (cont.)

4 7 0	122	106	7 6 0	31	27
4 9 0	66	— 67	7 8 0	54	37
4,11, 0	68	— 68	7,10, 0	43	— 45
4,13, 0	55	47	8 2 0	27	37
5 1 0	61	— 59	8 4 0	60	77
5 3 0	137	151	8 6 0	71	74
5 5 0	131	125	8 8 0	21	18
5 7 0	24	— 25	8,10, 0	—	9
5 9 0	22	— 24	8 1 0	104	—100
5,11, 0	96	112	8 3 0	72	— 85
5,13, 0	86	101	8 5 0	94	89
5 2 0	88	— 78	8 7 0	65	66
5 4 0	39	— 32	8 9 0	76	— 80
5 6 0	95	83	9 1 0	37	— 40
5 8 0	—	1	9 3 0	100	110
5,10, 0	59	— 48	9 5 0	103	117
5,12, 0	11	— 22	9 7 0	20	— 31
6 2 0	66	58	9 2 0	103	105
6 4 0	58	60	9 4 0	29	— 31
6 6 0	78	80	9 6 0	71	— 81
6 8 0	63	47	9 8 0	11	12
6,10, 0	36	30	10, 2 0	50	57
6,12, 0	40	53	10, 4 0	7	— 3
6 1 0	92	98	10, 1 0	—	8
6 3 0	66	70	10, 3 0	14	29
6 5 0	95	— 90	0 1 1	47	— 69
6 7 0	88	— 85	0 3 1	47	— 52
6 9 0	96	99	0 5 1	24	22
6,11, 0	65	66	0 7 1	35	— 28
7 1 0	123	131	0 9 1	79	— 73
7 3 0	24	32	0 11, 1	31	— 18
7 5 0	23	13	0 13, 1	16	4
7 7 0	98	109	0 15, 1	25	— 33
7 9 0	96	118	0 2 2	78	— 86
7,11, 0	—	0	0 4 2	295	—336
7 2 0	47	— 42	0 6 2	92	— 93
7 4 0	—	— 1	0 8 2	44	34

Table 2. (cont.)

0	10,	2	57	— 38	0 5 7	8	16
0	12,	2	104	—129	2 0 1	44	— 74
0	14,	2	66	— 81	4 0 1	—	8
0	1	3	16	8	6 0 1	24	18
0	3	3	42	28	8 0 1	44	— 34
0	5	3	18	24	10 0 1	39	— 24
0	7	3	11	10	2 0 2	60	— 93
0	9	3	37	36	4 0 2	46	39
0	11,	3	44	30	6 0 2	71	— 71
0	13,	3	—	9	8 0 2	139	—131
0	2	4	80	68	10 0 2	13	15
0	4	4	96	— 81	2 0 3	48	60
0	6	4	80	71	4 0 3	33	— 27
0	8	4	223	222	6 0 3	32	— 13
0	10,	4	49	44	8 0 3	12	8
0	12,	4	58	— 62	2 0 4	77	— 70
0	1	5	63	— 53	4 0 4	132	134
0	3	5	40	— 35	6 0 4	51	48
0	5	5	45	43	8 0 4	19	14
0	7	5	18	— 18	2 0 5	45	— 46
0	9	5	73	— 74	4 0 5	14	10
0	11,	5	13	— 8	6 0 5	22	26
0	2	6	53	45	8 0 5	44	— 45
0	4	6	168	—173	2 0 6	99	—106
0	6	6	79	— 77	4 0 6	22	14
0	8	6	17	19	6 0 6	75	— 61
0	1	7	10	2	2 0 7	52	47
0	3	7	18	12	4 0 7	36	— 21

Structure description

The crystal structure of antlerite is illustrated in Fig. 4, and the interatomic distances and angles are given in Table 3.

There are two types of non-equivalent copper atoms having different environments, viz. one is coordinated by four hydroxyl groups approximately coplanar at the corners of a rectangle and by one

Table 3. Interatomic distances and angles.

Distances in polyhedrons.

Cu (1) octahedron	
Cu (1)-OH(3)′	1.96 Å.
Cu (1)-OH(3)	2.06
Cu (1)-OH(1)	2.30
Cu (1)-O (2)	2.49
OH(3)-OH(3)′	2.64
OH(3)-OH(3)	2.82
O (2)-OH(3)′	2.90
O (2)-OH(3)	3.43
OH(1)-OH(3)	2.69
OH(1)-OH(3)′	3.43

Cu(2) octahedron	
Cu (2)-O (3)	1.90 Å.
Cu (2)-OH(2)	1.96
Cu (2)-OH(1)	1.97
Cu (2)-OH(3)	1.97
Cu (2)-O (1)	2.33
Cu (2)-O (2)	2.37
O (3)-OH(2)	2.63
O (3)-OH(1)	2.86
OH(3)-OH(1)	2.69
OH(3)-OH(2)	2.96
O (1)-O (3)	2.90
O (1)-OH(1)	3.08
O (1)-OH(3)	3.09
O (1)-OH(2)	3.11
O (2)-OH(3)	2.90
O (2)-OH(2)	3.00
O (2)-OH(1)	3.06
O (2)-O (3)	3.32

SO_4 tetrahedron	
S -O(1)	1.50 Å.
S -O(2)	1.48
S -O(3)	1.52
O(1)-O(2)	2.47
O(1)-O(3)	2.44
O(2)-O(3)	2.46
O(3)-O(3)	2.46

Distances between different polyhedrons	
O (3)-OH(3)′	2.94 Å.
O (3)-OH(1)′	3.15
O (3)-OH(2)′	3.32
O (3)-O (3)′	3.76
OH(3)-OH(2)′	3.17
OH(3)-O (1)′	3.26
OH(2)-OH(1)′	3.60

Angles in copper octahedrons	
∠OH(3) -Cu(1)-OH(3)	102.4°
∠OH(3)′-Cu(1)-OH(3)′	87.7
∠OH(3) -Cu(1)-OH(3)′	82.6
∠OH(3) -Cu(1)-O (2)	99.2
∠OH(3)′-Cu(1)-O (2)	80.1
∠OH(3) -Cu(1)-OH(1)	76.0
∠OH(3)′-Cu(1)-OH(1)	106.8
∠O (3) -Cu(2)-OH(1)	93.0
∠O (3) -Cu(2)-OH(2)	83.3
∠OH(3) -Cu(2)-OH(1)	86.3
∠OH(3) -Cu(2)-OH(2)	97.6
∠O (1) -Cu(2)-OH(1)	91.3
∠O (1) -Cu(2)-OH(2)	92.4
∠O (1) -Cu(2)-OH(3)	91.5
∠O (1) -Cu(2)-O (3)	83.8
∠O (2) -Cu(2)-OH(1)	89.3
∠O (2) -Cu(2)-OH(2)	87.3
∠O (2) -Cu(2)-OH(3)	83.4
∠O (2) -Cu(2)-O (3)	101.5

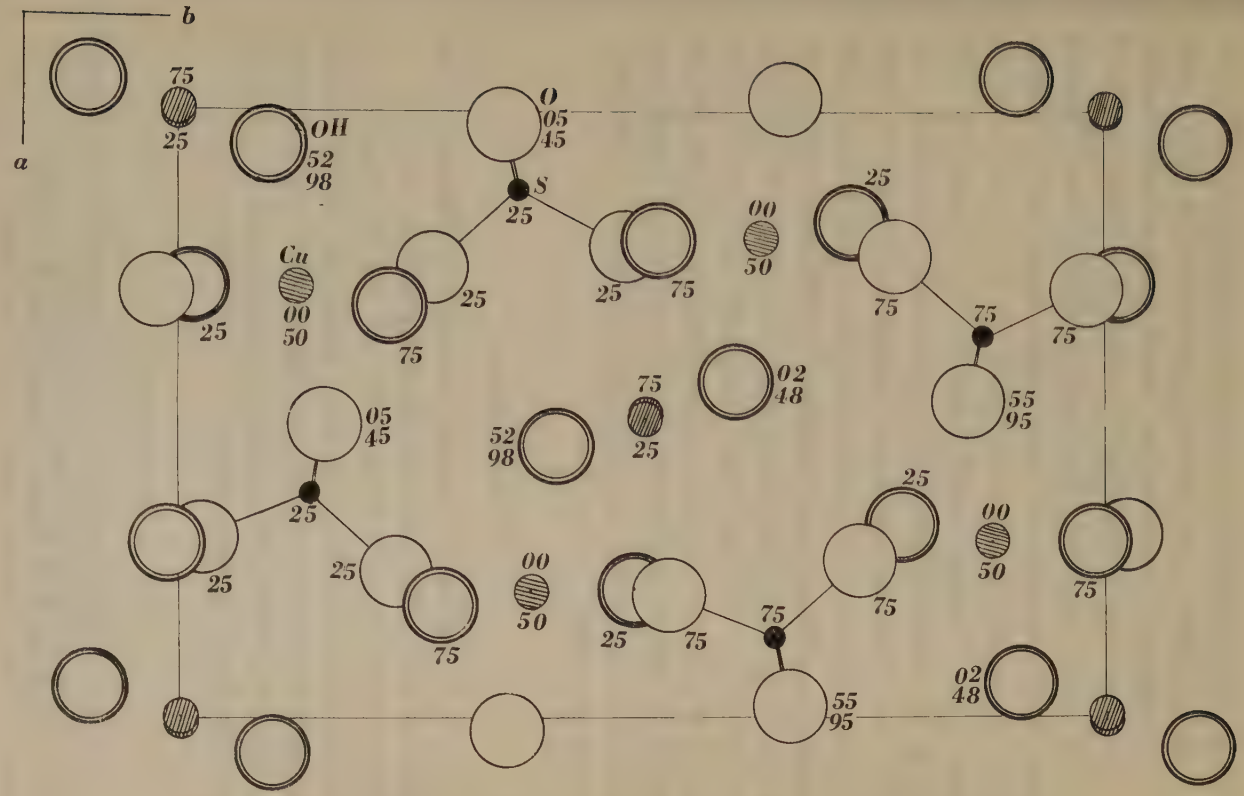

Fig. 4. The structure of antlerite projected on the (001) plane. Numbers give the height of atoms in decimal fractions of the *c*-length.

hydroxyl group and one oxygen atom at a greater distance, and the other is surrounded by three hydroxyl groups and one oxygen atom nearly in a plane and by two oxygen atoms at a greater distance nearly at a right angle to this plane. The spatial arrangement around the copper atoms completes distorted octahedral groups which are connected with one another to form copper-oxygen and/or copper-hydroxyl sequences stretching along [001].

Two types of copper atoms found in this structure has been known in an analogous fashion in the structure of malachite[9] and azurite[8]. But a trigonal bipyramidal arrangement of nearest neighbours around the divalent copper atoms as found in some basic copper oxysalts such as olivenite and libethenite[9], in which one-half of the copper atoms are octahedrally coordinated, is not found in the structure of antlerite. The octahedral arrangement around the copper atoms described above is, however, similar with those in the halogen compounds of divalent copper atom like atacamite[8] and other cupric halides as well as in basic oxysalts such as lindgrenite[2] and above-mentioned minerals.

Acknowledgements

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ABNORMAL OPTICAL PROPERTIES OF BABINGTONITE FROM THE YAKUKI MINE, JAPAN*

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Abstract

Abnormal optical properties of babingtonite from the Yakuki mine, Japan, are described. Sections cut nearly normal to each of the optic axes of this mineral show no extinction. This is probably due to elliptic vibration of light which passes through the sections. Dependence of the ellipticity on the orientation of the section was determined. Interference figure exhibited by sections cut nearly normal to one of the optic axes is anomalous, especially remarkable for red light. The mineral absorbs light of different colour in different amount. Dependence of the optical density on the wave lengths of light is shown by variation curves.

Introduction

In 1922, Manjiro Watanabe[6] described babingtonite from the Yakuki mine, Fukushima Prefecture, Japan. He gave detailed morphological data, taking the crystallographic axes after Dauber[1]. Later, Richmond[3] adopted a new axial system of babingtonite according to the normal triclinic setting proposed by Peacock[2], and gave the optical orientations of the mineral. Further, he gave the chemical formula of the mineral as $Ca_4Fe_2^{2+}Fe_2^{3+}Si_{10}O_{28}(OH)_2$ on the basis of its chemical analysis.

Recently, the present writer made some optical examination of

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babingtonite from the Yakuki mine, and determined its orientations.

In the course of his study, he found that sections cut nearly perpendicular to each of the optic axes (within the range of about 20° from the optic axis) generally show no extinction, even observed with monochromatic light, and confirm that this phenomenon is due to elliptic vibration of light that passes the mineral in the above-said direction, as the present writer[4)5)] has remarked of some alkali amphiboles in his previous papers. In the present paper, the writer intends to give a brief description of the abnormal optical phenomenon of babingtonite.

Morphology and optical orientation

Morphological and optical data of babingtonite as obtained by the writer and Richmond[3)], are compared in Table 1. The writer's data are based on his study of specimens, about 1~3 mm. in size. They are prismatic, with faces belonging to [001]; cleavage: perfect {001} and indistinct {110}.

Table 1. Morphological and optical data of babingtonite.

(*h k l*)	Yakuki (Shoda)			Blueberry Mt. (Richmond)	
	ρ	φ	*n*	ρ	φ
(010)	90°00′*	0°00′*	7	90°00′	0°00′
(110)	90 05	47 38	4	„	47 36
(100)	90 00	75 47	7	„	75 49
(1$\bar{1}$0)	89 56	112 04	8	„	112 11
(1$\bar{2}$0)	89 52	136 21	5	„	136 54
(001)	4 25	57 19	4	4 36	56 39
+A	22°	−2°		20°55′	−5°48′
+B	86	52		86 42	53 20

n: Number of faces measured. * Standard point.

With sections cut nearly normal to each of the optic axes, the orientations of the optic axes with respect to the normals of the

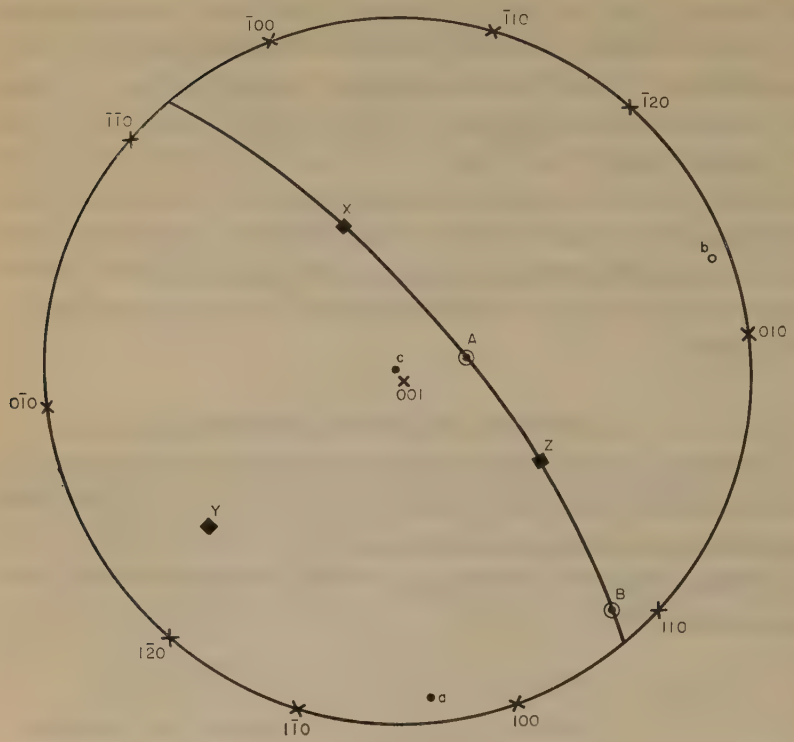

Fig. 1. Stereographic projection showing the optical orientation of Yakuki babingtonite.

sections were determined conoscopically. The results were plotted in stereographic projection as shown in Fig. 1.

Confirmation of elliptic vibration

A section of an aggregate of babingtonite crystals was examined under the microscope, and a comparatively large grain of the mineral which shows no extinction was selected for optical study. In order to confirm the elliptic vibration of light passing through the grain, it was observed between two $\frac{1}{4}\lambda$ plates, superposed in subtraction position, using the polarizing microscope with three rotation stages,

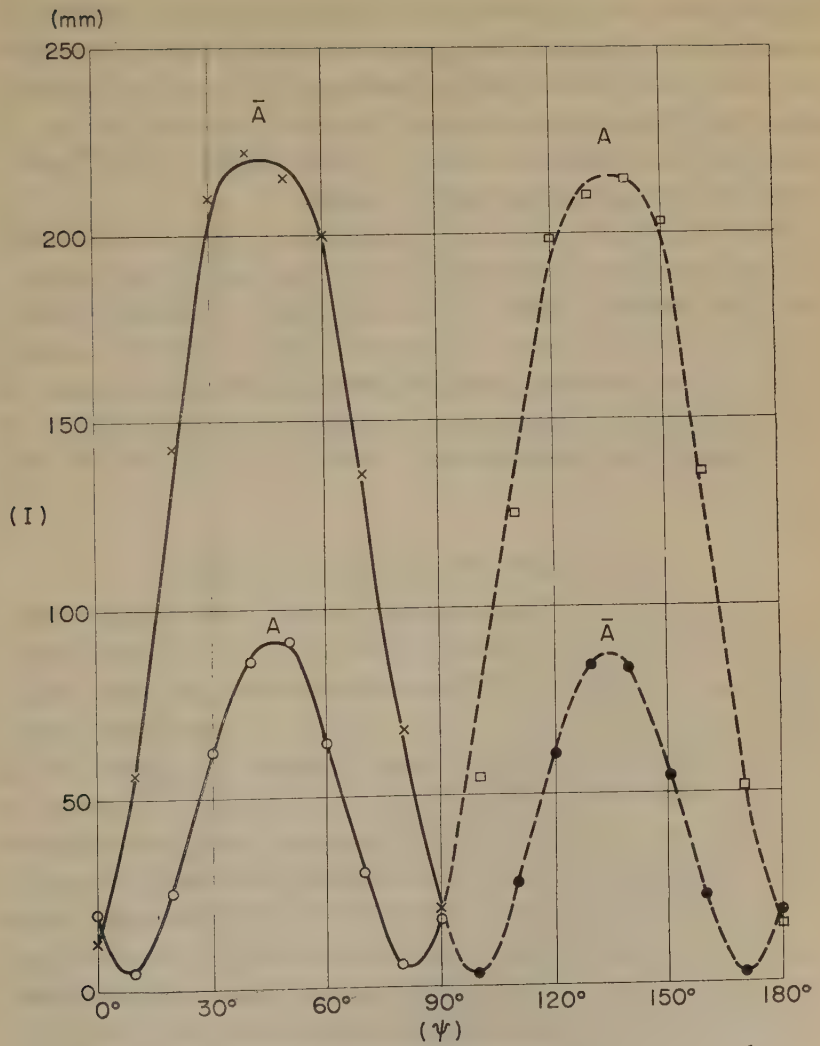

Fig. 2. The values of the minimum intensity for various values of Ψ for the section near the optic axis A (crossed polars).
Full lines: for the right-handed incident polarization.
Broken lines: for the left-handed incident polarization.
□ and ○: for sections nearly normal to +A.
× and ●: for section nearly normal to −A.
I: Scale readings on galvanometer.

and the intensity of light transmitted through the grain was measured by means of the photomultiplier-galvanometer-set[4]. Then, the section was turned over and the similar measurement was made for the same grain but in the opposite direction. The result is shown in Fig. 2, where full line represents the curve for right handed incident polarization, and broken line, for the left handed.

From this figure, it is readily seen that the sence of the elliptic vibration is reversed if viewed from the other side of the crystal, while the ellipticity (ratio of the axial lengths of ellipse) remains constant. From the above, it is probable that non-extinction phenomenon of this mineral is related to a centrosymmetrical one and is due to the elliptic vibration of light caused by strong absorption of this mineral. (The orientation and the value of ψ ($=+8°$) for this grain is shown in Fig. 3.)

Dependence of the ellipticity on orientation

It is very easy to distinguish optic axis A from B by observing interference figure, of which explanation will be given later. Moreover, it is possible to decide whether the optic axis under observation corresponds to +A or −A in direction by determining relative orientations of (1) the optic axis under question, (2) normal of the cleavage plane ({001} and/or {110}) and (3) bisectrix Y (normal of the optical plane). With twenty-five grains, cut nearly perpendicular to the optic axis, which had been selected under the microscope, accurate determinations were made of their orientations with respect to the optic axis and optical plane, by means of the universal stage. Then, the ellipticity of vibration for each of these grains was determined by the method already described.

Observations were made with grains orientated near the optic axis, in either sense, +A or −A. The results obtained are shown in Fig. 3, all reduced to those in +A sence. In Fig. 3, solid circles, solid squares and solid triangles represent directions with elliptic vibration of positive sign (right handed), the values of ψ (a measure of ellipti-

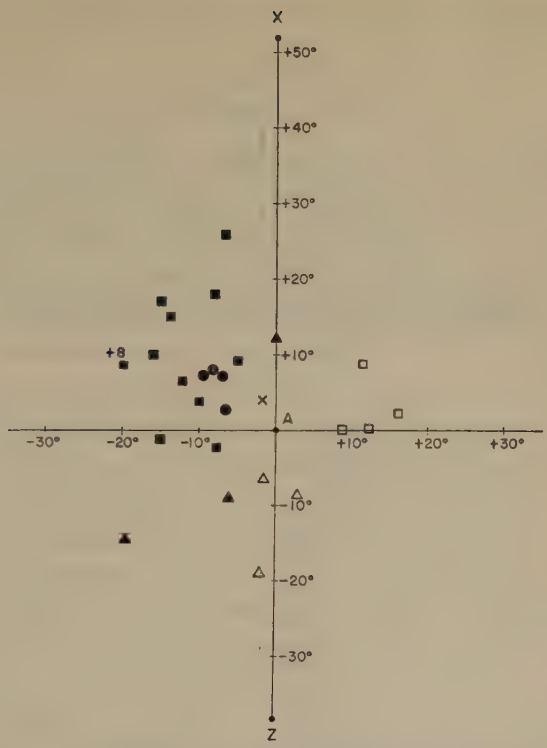

Fig. 3. Dependence of the ellipticity of vibration on orientation near the optic axis A.

Circle:	$\Psi_{min}>10°$	Cross:	$2°>\Psi_{min}>-2°$.
Square:	$10°>\Psi_{min}>5°$	Solid:	Right handed.
Triangle:	$5°>\Psi_{min}>2°$	Open:	Left handed.

city) being respectively $\psi_{min}>10°$, $10°>\psi_{min}>5°$ and $5°>\psi_{min}>2°$. The ψ is the angle between the vibration direction of polarizer and one of the vibration directions of the superposed $\frac{1}{4}\lambda$ plates, and is related to ellipticity ε as follows;

$$\varepsilon=\tan\psi\,.$$

Open circles, open squares and open triangles represent directions with elliptic vibration of negative sign (left handed), and crosses represent directions with nearly linear vibration ($2°>\psi_{min}>-2°$).

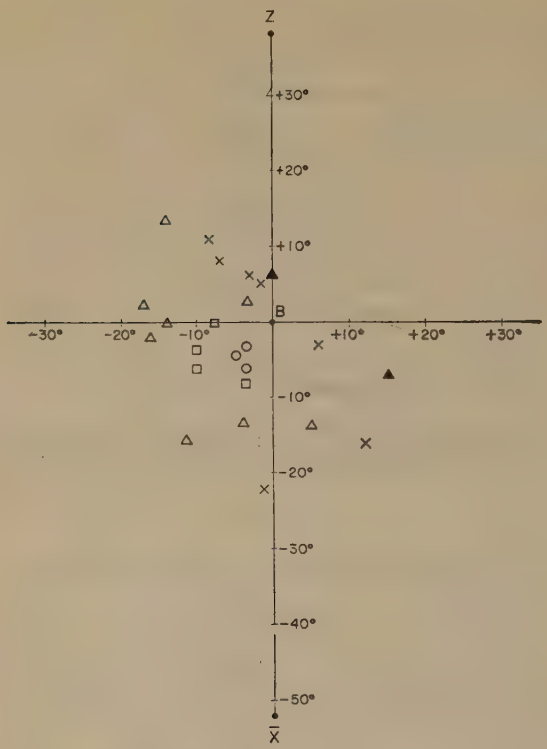

Fig. 4. Dependence of the ellipticity of vibration on orientation near the optic axis B. Notation is the same as Fig. 3.

The region near the optic axis A is divisible into two parts, one for the right handed vibration, and the other, for the left handed. The two parts are bounded by a line, representing directions for linear vibration, which probably runs from upper-right through A to lower-left of the figure at a small angle to the trace of the optical plane.

Fig. 4 shows the results of similar measurements made in the directions near the optic axis B. From this figure, it may be seen that, for the light passing in direction near the optic axis B, the ellipticity tends to be smaller than that for the light near A. Here,

the boundary line between the two parts near B runs probably from upper-left to lower-right.

Interference figure

The interference figure observed with sections normal to the optic axis A of babingtonite is peculiar in certain respects. With a section nearly normal to the optic axis A, at the parallel position, a usual black isogyre is seen, crossing the field of view parallel to the vibration direction of polarizer or analyzer. However, instead of isochromatic rings, as ordinarily seen with transparent minerals, there appear rings consisting of various colours; thus, a certain part of one ring is deep green, while the remaining part is faintly coloured, as is illustrated in Fig. 5 (a), Plate I. At the diagonal position, the isogyre changes from black to red, while the deep green part shows no change in colour, as is illustrated in Fig 5 (b), Plate I.

With a monochromatic red light, the above-said deep green portion of the ring is replaced by a dark arc, and the remaining portion is seen only weakly lighted, as shown in Fig. 5 (c), Plate I. With gradual change of colour of light toward blue, the dark arc extends along the ring, and finally, with blue light, dark part forms one continuous ring (Fig, 5 (e), Plate I). At the diagonal position, with red light, the isogyre is obscure (Fig. 5 (d), Plate I). With change of colour as above, the isogyre becomes more and more distinct (Fig. 5 (f), Plate I).

The interference figure for sections nearly normal to the optic axis B is not so peculiar as that for sections normal to A. The isogyre is less clearly seen than in the ordinary case.

Although a thorough explanation of the above peculiar features of the interference figure is not at hand, this may be due to elliptic vibration of light and its strong absorption variation near the optic axis.

Absorption and pleochroism

Pleochroism was observed with grains, orientated practically perpendicular to each of the bisectrices X, Y and Z, with the following result. Z....pale brown, Y....lilac, X....deep green.

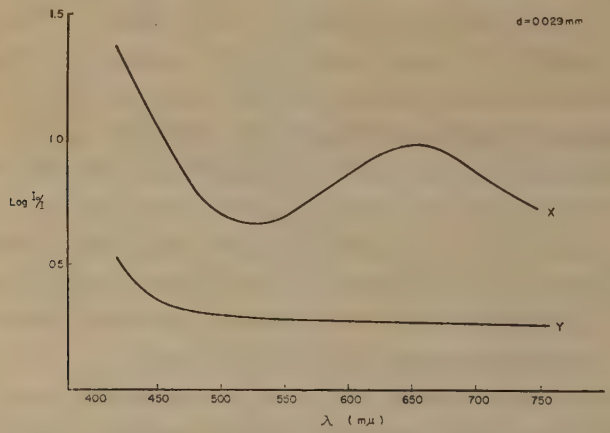

Fig. 6. Variation of the optical density with wavelength for the section practically normal to Z.

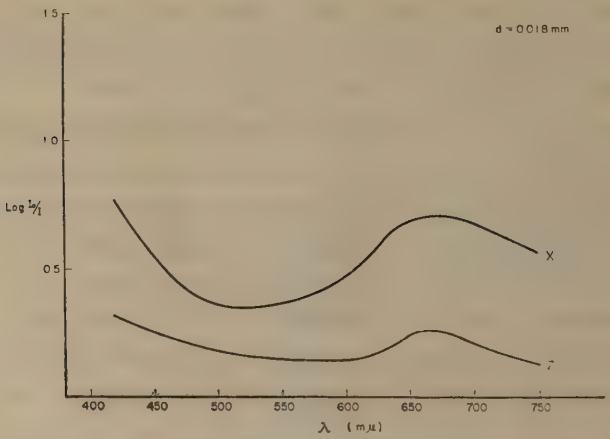

Fig. 7. Variation of the optical density with wavelength for the section practically normal to Y.

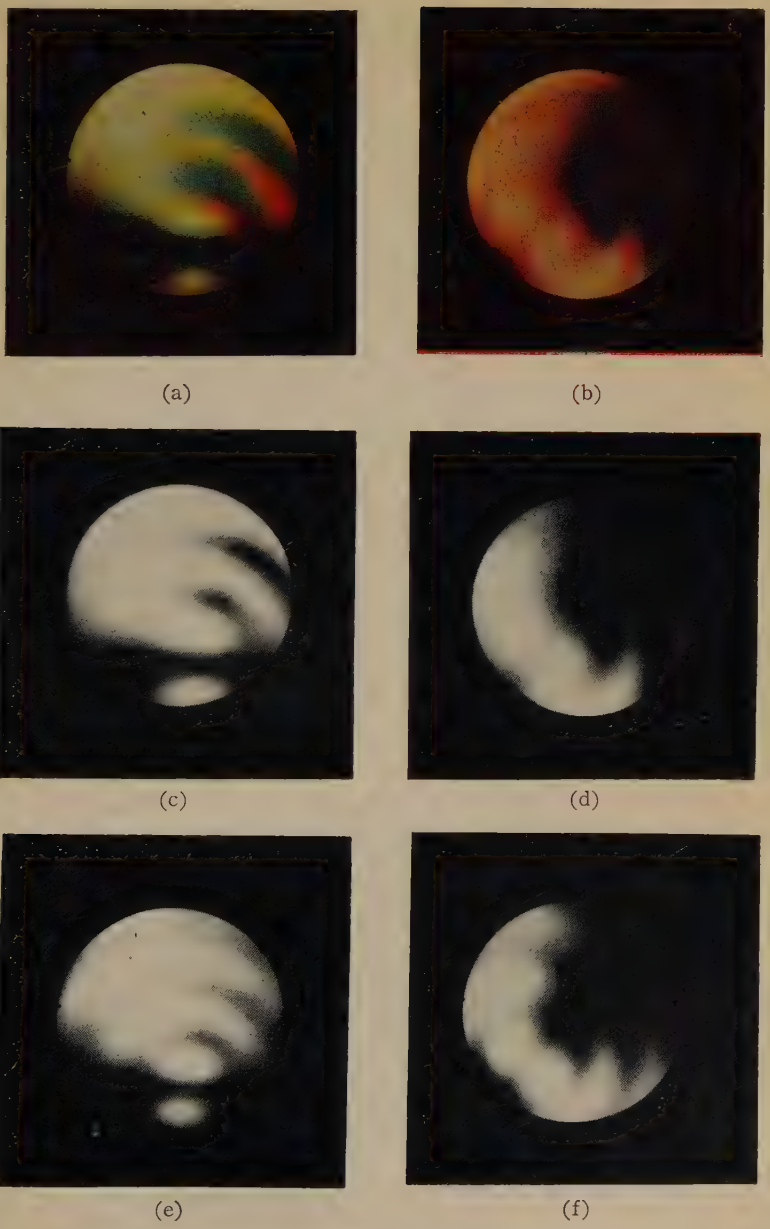

Fig. 5. Interference figure for a section nearly normal to the optic axis A of Yakuki babingtonite. (a), (b) with white light. (c), (d) with red light. (e), (f) with blue light.

The variation of optical density with wavelength for these grains was photometrically determined, kindly for the writer, by J. Tanaka. The results are shown in Figs. 6 and 7. It is seen from these figures that the curve for the vibration parallel to X has a distinct maximum at the position corresponding to the wavelength of about 600 mμ. The curve for the vibration parallel to Z also has a maximum at the same position as for X, though less remarkable, while the curve for Y has no appreciable maximum within the range of visible light.

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The writer wishes to express his thanks to Emeritus Prof. S. Tsuboi for reading the manuscript with criticism. He also thanks Prof. R. Sadanaga, of this Institute, and Profs. N. Katayama and S. Iwao, College of General Education who made facilities available for this study. He is also indebted to Mr. M. Nishiwaki, the head of the Yakuki mine, who offered the valuable specimen of babingtonite. Special thanks are due to Dr. J. Tanaka of the Institute for Solid State Physics, University of Tokyo for the optical experiments on light absorption. For preparation of sections, the writer is indebted to Mr. T. Watanabe of the Earthquake Research Institute.

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MINERALOGICAL ABSTRACTS

FROM

THE SCIENTIFIC PAPERS PUBLISHED

IN JAPAN

Age determination and isotope mineralogy: 3076–3077, apparatus and techniques: 3078, book notices: 3079, clay minerals: 3080–3083, economic minerals and ore deposits: 3084–3092, experimental mineralogy: 3093, geochemistry: 3094–3095, mineral data: 3096 3111, new minerals: 3112, physical properties of minerals: 3113, rock-forming minerals and petroloy: 3114–3119, topographical mineralogy: 3120–3121, various topics: 3122.

Age Determination and Isotope Mineralogy

3076. **Saito (Nobufusa), Tatsumi (Tatsuo) and Sato (Kazuo):** *Absolute age of euxenite from Antarctica.* Antarctic Record, Repts. Jap. Antarctic Res. Exped., No. 12, 31–36 (1961).

Absolute age of the euxenite [3120], which was collected from a granite pegmatite at Skallen on the eastern coast of Lützow-Holm Bay, has been determined by the U-Pb method. The average of the $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$ and $^{207}Pb/^{206}Pb$ ages was found to be 470×10^6 years, while the $^{208}Pb/^{232}Th$ age was as young as 375×10^6 years.

3077. **Yamaguchi (Masaru):** *Alpha-activity of granite and andesite zircons from Southwest Japan measured with nuclear emulsion.* Mem. Fac. Sci., Kyushu Univ., Ser. D, 11, 49–59, 3 figs. (1961).

Number of alpha particles emitted from each minute grains of zircon separated from several granites and a hornblende andesite from Southwest Japan have been counted with the Fuji ET-2E stripping type nuclear emulsion. Since the alpha tracks are easily correlated with crystal features of zircons under the microscope, the alpha-activity was effectively used as a guide in classifying this mineral into several types.

Cretaceous granites in Southwest Japan contain zircons variable in colour, crystal habit and alpha-activity. Zircons associated with monazite or thorite in some granites are less radioactive than usual zircons.

Apparatus and Techniques

3078. **Morita (Kiyoshi):** *A spectrographic determination of lead*

in zircon. Repts. Government Indust. Res. Inst., Nagoya, **9**, 571–574, 4 figs. (1960). (Japanese with English abstract.)

Spectrographic analyses of lead in zircon were carried out in the following way, using JACO grating spectroscope. As the base and the internal standard, silica and indium were used respectively, and the samples were excited by D. C. arc. The line pairs selected were Pb(I) 2833.1Å. and In(I) 2932.6Å. The results were compared with those obtained by dithizone method, with satisfactorily good agreement. The method is applicable to samples containing lead from 5 to 1000 ppm. with an accuracy of about 1～7% of the amount present. The accuracy is within 28% of the amount present for samples as low as 1ppm.

Book Notices

3079. **Committee for the Study of Uranium and Thorium Minerals, Tokyo** (Chairman: **Katayama (Nobuo)**: *Uranium, Its Resources and Minerals.* 558 pp., 9 pls., 1 map (1961), Asakura Publishing Co., Ltd., Tokyo, 3500 Yen. (in Japanese.)

It contains (A) reviews on uranium problems of the world, (B) papers on selected topics, (C) descriptions on uranium minerals from Japan and (D) descriptions on uranium deposits in Japan. The selected topics are as follows; B I. *Genesis of uranium deposits in sedimentary rocks,* by **Katayama (Nobuo)**; B II. *Relationship between massif and uranium deposits,* by **Sato (Motoo)**; B III. *Distribution of radioactivity in granites,* by **Hatsuda (Zin'ichiro)**; B IV. *Uranium in granites,* by **Hayase (Ichikazu)**; B V. *Mode of occurrence of uranium minerals in pegmatite,* by **Omori (Keiichi)**; B VI. *Mode of occurrence and genesis of the uranium accompanying bedded manganese deposits,* by **Watanabe (Takeo)**; B VII. *Environment of formation of ningyoite,* by **Muto (Tadashi)**; B VIII. *Uran-mica group,* by **Henmi (Kitinosuke)**; B IX. *Fixation of uranium by clay minerals through ion exchange,* by **Ukai (Yasuo)** and **Yokoi (Toshio)**; B X. *A rapid microanalytical method for uranium determination applying paper chromatography,* by **Sakanoue (Masanobu)**; B XI. *Recovery of uranium by chlorination method,* by **Suzuki (Takamura)**; B XII. *Leaching of uranium from monazite,* by **Nishimura (Shin'ichi)**; B XIII. "*U-scope*", by **Takahashi (Kikuo)** and **Okada (Shigeru)**.

Clay Minerals

3080. **Muchi (Masatomo)**: *Some shapes of halloysite and montmorillonite in tuffaceous rocks from Kyushu.* Bull. Fukuoka Gakugei Univ., **9**, 43–66, 23 figs. (1959). (in Japanese.)

Halloysite and montmorillonite found in tuffaceous rocks in Kyushu were examined by X-ray analysis, d. t. a., and electron microscope. Metahalloysite occurs in fibrous or edge curled lath-shaped particles and is considered to be a dehydrated product of poorly crystallized hy-

drated halloysite. Montmorillonite occurs in poorly defined flakes and sometimes in ball-like shaped habit resembling those of halloysite and allophane.

3081. **Kato (Toshio) and Minato (Hideo):** *Deweylite from the Akaishi Mine, Ehimé Prefecture.* Kobutsugaku Zasshi, **5**, 11–24, 4 pls., 5 figs. (1960). (in Japanese.)

Pale brown to pale yellow mass of deweylite occurs in the fracture of the serpentine rock from the Akaishi mine. The results of X-ray diffraction, d. t. a., electron micrographs, infra-red spectra and chemical analyses are given with those for several specimens from other localities. Deweylite appears to contain surplus water and consist of at least two types of layer silicates, platy serpentine and talc.

Chemical analysis by T. Kato gave SiO_2 44.27, Al_2O_3 1.18, Fe_2O_3 0.36, FeO 2.73, CaO 0.41, MgO 32.11, K_2O 0.17, Na_2O 0.20, $H_2O(+)$ 10.74, $H_2O(-)$ 8.17, total 100.34%.

3082. **Sugimura (Takashi):** *The effect of iron and alkalies on the thermal change of kaolinitic clays.* Kobutsugaku Zasshi, **5**, 89–99, (1961). (in Japanese.)

Studies on Syudei-yaki which is a kind of chinaware made by firing Syudei-do, a kaolinitic clay from Tokonamé, Aichi Prefecture, revealed the following.

(1) The raw material is composed of iron-rich montmorillonite, hydrated halloysite, and small amounts of quartz and feldspar.

(2) The fired products consist of mullite, hematite and small amounts of quartz and vitrified feldspar. Mullite is well crystallized at 1200°C., about 300°C. lower than in the case of kaolinite, whereas the conversion of hematite to magnetite does not take place up to that temperature. It is suggested that the presence of alkalies and iron as well as firing at lower temperature have brought about the strength and beautiful apperance in Syudei-yaki.

3083. **Kizaki (Yoshio):** *The clay minerals in mudstones of the Tertiary beds from Yokokawa, Gunma Prefecture.* Mem., Gunma Univ., **9**, 1–12, 7 figs. (1961). (Japanese with English abstract.)

A clay occuring in mudstones of the Tertiary formations near Yokokawa has a 13.4Å. basal spacing: glycerol and $CaCl_2$ treatments increase this to 18.4Å. and 15.8Å. respectively. X-ray analysis of the orientated aggregates revealed that the mineral is a randomly interstratified two water layer montmorillonite (15.4Å.)-one water layer montmorillonite (12.4Å.), with the ratio of 4 : 6 in amounts. This ratio coincides with that of total exchangeable divalent cations to monovalent cations.

Economic Minerals and Ore Deposits

3084. **Honda (Sakurô):** *Mineralogical studies of Gojônomé stoneware clay and Shiroiwa stoneware clay in Akita Prefecture.* Repts. Research Inst., Underground Resources, Mining

Col., Akita Univ., No. 21, 7–15, 4 pls., 7 figs. (1959). (Japanese with English abstract.)

X-ray, thermal and chemical analyses and swelling tests were made of stoneware clays from Gojônomé and Shiroiwa.

(1) Gojônomé stoneware clay is an alluvium clay and composed of montmorillonite and a small amount of kaolin mineral associated with quartz and feldspar.

(2) Shiroiwa stoneware clay belonging to either an alluvium clay or deluvium clay consists of hydrated and dehydrated kaolin minerals, quartz, feldspar and α-cristobalite.

3085. **Tanaka (Nobuya)**: *Economic geological study of clay minerals.* Kyushu Kozan Gakkaishi, **28**, 235–252, 283–294, 333–347, 31 figs. (1960). (Japanese with English abstract.)

Studies on the clay minerals such as kaolinite, and Ca-, K- and Fe^{3+}- montmorillonite found in the coal-bearing Tertiary formations in Kasuya Coal Field enabled precise classification of the stratigraphy of the coal seams and strata. X-ray powder, differential thermal and chemical data, and consideration on the sedimentary environment and palaeo-geography of the area are given.

3086. **Omori (Keiichi), Seki (Toshikazu) and Sakamoto (Takeshi)**: *X-ray studies on bentonites from Kaminoyama, Yamagata Prefecture.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., **45**, 81–88 (1961). (Japanese with English abstract.)

By the X-ray diffraction charts, bentonites from Kaminoyama, Yamagata Prefecture, are divided into the following four types, (1) montmorillonite, as essential mineral, with a little zeolite (clino-ptilolite), plagioclase and cristobalite, (2) zeolite with montmorillonite, plagioclase and cristobalite, (3) zeolite with montmorillonite, plagioclase, cristobalite and orthoclase, (4) montmorillonite and celadonite with zeolite, plagioclase and cristobalite. Types (1) and (2) occur widely while type (4) is a new occurrence in this area.

3087. **Abe (Masahiro)**; *Consideration on the organic constituents of the source-rock of petroleum at the eastern foot of Chokai Volcano... Studies on the source rock of petroleum* (7th report). Jour. Jap. Asso. Min. Petro. & Econ. Geol., **45**, 17–24 (1961). (Japanese with English abstract.)

The Tertiary sediments distributed widely at the eastern foot of Chokai Volcano, Akita Prefecture are chemically analysed. The relationship between the organic constituents of the fine grained clastic sediments and the source of oil is discussed.

3088. **Narita (Eikichi) and Hirama (Masao)**: *Magnetite and other iron oxide minerals of the Katsuraoka mineralized zone, Hokkaido.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., **45**, 25–30 (1961). (Japanese with English abstract.)

The mineral assemblages accompanying magnetite of the area are spinel-pyroxene-biotite, garnet-diopside and actinolite-epidote-quartz-sulphides. The chemical composition, lattice constants and minor elements of magnetites are studied.

3089. **Harada (Zyunpei):** *Manganese ore minerals from Hokkaido, Japan.* Mining Geol. (Japan), Tenth Anniv. Vol., 319–325, 9 figs. (1961). (Japanese with English abstract.)

A brief summary of the results of mineralogical investigations on manganese ore minerals from Hokkaido, Japan, which have been carried out at the writer's institute, is given, including descriptions on alabandite, rhodochrosite, Mn-calcite, pyrolusite, cryptomelane, ramsdellite, manganese wad, todorokite, psilomelane, manganite, groutite, hausmannite, tephroite, rhodonite, inesite, penwithite, braunite. The d. t. a. curves for cryptomelane, manganese wad and manganite, and two crystal figures of manganite are given as well.

3090. **Ishibashi (Masao) and Sasaki (Satoshi):** *On some silver-lead-zinc ores from the Toyoha mine, Hokkaido, Japan.* Mining Geol. (Japan), Tenth Anniv. Vol., 337–343, 13 figs. (1961). (Japanese with English abstract.)

Ore minerals of the Toyoha deposits, which consist of fissure-filling Ag-Pb-Zn veins in green rocks of the Miocene age, are studied by means of ore microscopy. Main ore minerals are pyrite, galena, sphalerite, with quartz, rhodochrosite, rhodonite and chlorite as gangue minerals. Small amount of argentite, pyrargyrite, As-polybasite, stephanite, miargyrite, marcasite, pyrrhotite, tetrahedrite, arsenopyrite and chalcopyrite also occur in the deposits. Secondary minerals are hematite, magnetite, chalcocite, covelline and native silver. It is also described that the Toyoha deposits are typical ones of the Pb-Zn-pyrite deposits in South-West Hokkaido, and that they have been altered by the action of meteoric water.

3091. **Kato (Toshio):** *A study on the so-called garnierite from New Caledonia.* Miner. Jour., 3, 107–121, 2 pls., 4 figs. (1961).

Fourteen samples of the so-called garnierite from New Caledonia have been examined by means of X-ray diffraction, electron microscopy and diffraction, chemical and spectrochemical analyses, infrared absorption, differential thermal analysis and heat treatment. The presence of antigorite (platy serpentine), "talc", chrysotile (fibrous serpentine) and chlorite type minerals has been affirmed. The results of chemical analysis, infrared absorption and differential thermal analysis correlate to those structural types. Neither sepiolite nor nickel-bearing saponite, pimelite, has been found. Especially, the common occurrence of pimelite is rather doubtful. The results of attempt to synthesize nickel hydrosilicate are also presented.

3092. **Hayashi (Hisato):** *Mineralogical study on alteration pro-*

ducts from alteration aureole of some "Kuroko" deposits. Kobutsugaku Zasshi, 5, 101–125, 8 figs. (1961). (Japanese.)

Optical microscopy, X-ray diffraction, d. t. a. and wet chemical analyses on the minerals of altered aureole of "kuroko" deposits at the Hanaoka mine, Akita Prefecture, the Kamikita mine and the Otaki mine in Aomori Prefecture, Japan, revealed that there are two different types of altered aureole namely the one mainly consisting of sericite and chlorite and the other consisting of pyrophyllite, kaoline minerals and diaspore. Regular mixed-layer minerals of chlorite-montmorillonite and of sericite-montmorillonite, irregular mixed-layer mineral of sericite-montmorillonite were found at the Hanaoka mine, and regular mixed-layer mineral of sericite-montmorillonite at the Kamikita mine as well.

Experimental Mineralogy

3093. **Omori (Keiichi) and Nakashima (Tsuyoshi):** *Mullite in porcelain bodies.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., 45, 201–208 (1961). (Japanese with English abstract.)

Mullite in porcelain bodies heated at 1300°C. was studied by means of electron micrographs, X-ray powder diffractions and infrared absorption spectra. The mullite shows a strong absorption at 9.5μ. and a medium absorption at 13.0μ. in the infrared spectra.

Geochemistry

3094. **Nambu (Matsuo) and Tanida (Katsutoshi):** *Progressive alteration of manganese dioxide observed at the Toyoguchi mine, Iwaté Prefecture.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., 45, 39–48 (1961). (Japanese with English abstract.)

The Toyoguchi deposit is one of the bedded manganese deposits in black banded chert of the Palaeozoic formation. Rhodochrosite has been altered to pyrolusite through bimessite and ramsdellite and to cryptomelane by the potassium absorption. The minerals are determined by chemical, X-ray and d. t. a. methods.

3095. **Takimoto (Kiyoshi) and Minato (Taneo):** *On the relationship between temperature-types of deposits and distribution of minor constituants in sulfide minerals.* Mining. Geol. (Japan), Tenth Anniv. Vol., 331–337, 8 figs. (1961). (Japanese with English abstract.)

The Se, Mn, Cd, Fe, Zn and S contents in 26 samples of sphalerite from the typical contact deposits of the Chichibu mine and the Kamioka mine are determined quantitatively by means of wet chemical analyses (Zn, S, Fe), polarographic method (Cd, Mn) and colorimetric method (Se). The ratios of S/Se, Zn/Mn, Zn/Cd and Zn/Fe are investigated in correlation with the type of ore deposits and especially with the temperature type. The results follow: (1) Se concentrates in high temperature deposits; (2)

Mn concentrates in low temperature deposits at the Chichibu mine and in high temperature deposits at the Kamioka mine, while Cd shows reverse relation; (3) Fe concentrates in high temperature deposits at the Kamioka mine, but no appreciable variation was observed at the Chichibu mine; (4) Fe increases as Mn increases while Cd decreases as Fe and Mn increase.

Lattice parameters of sphalerites are also measured and are correlated with Fe contents.

Mineral Data

3096–3100. **Kawai (Teikichi)**: *Chemical studies on minerals containing rarer elements from the Far East district.* Nos. 52–56. Nippon Kagaku Zasshi, **81**, 1218–1220, 1238–1239 (1960). (in Japanese.)

3096. (52) *Fergusonite from Suishoyama, Kawamata-machi, Fukushima Pref., Japan.* p. 1218.

Fergusonite from this locality associated with biotite and feldspar has already been described. One described here is a crystal found very seldomly in quartz crystals. Black, radioactive; sp. gr. 4.5, suffered no metamictization. Analyzed specimens were free from admixed black, fine grained uraninites. Chemical analysis gave MgO 1.34, CaO 1.15, MnO 1.94, Al_2O_3 0.26, Fe_2O_3 1.90, ΣY_2O_3 34.57, TiO_2 0.55, ThO_2 2.16, SnO_2 etc. 0.15, $(Nb, Ta)_2O_5$ 42.33, UO_2 5.70, UO_3 3.06, SiO_2 3.05, H_2O 2.16, total 100.32%.

3097. (53) *Zircon from Hikari Gold Mine, Sogawa-mura, Gifu Prefecture, Japan.* p. 1218.

White crystalline residue after panning of crushed gold quartz vein in the Palaeozoic slate was determined as zircon by X-ray examination. Cheminal analysis gave MgO 0.13, Al_2O_3 1.33, Fe_2O_3 5.30, TiO_2 0.17, $ThO_2+\Sigma Y_2O_3$ 0.76, ZrO_2 56.70, SiO_2 33.03, P_2O_5 1.75, H_2O 0.67, total 99.84%.

3098. (54) *Betafite from Kaijo (Hicheng), Manchuria.* p. 1219.

Very fine crystals of dark greyish betafite were found associated with euxenite, zircon, fergusonite and allanite in mica-bearing pegmatite at Kaijo. Observed crystal forms are *o*{111}, *d*{110} and *m*{311}, among which *o* is predominent and *d* and *m* are usually very small. The crystal is up to a few cm. in length and gave clear X-ray pattern hence not entirely metamictized. Strongly radioactive. Chemical analysis gave MgO 0.92, CaO 4.35, MnO 1.83, Al_2O_3 15.68, Fe_2O_3 2.76, $\Sigma Y_2O_3+ThO_2$ 1.56, SnO_2 etc. 7.94, TiO_2 14.88, $(Nb, Ta)_2O_5$ 11.54, UO_2 3.63, UO_3 18.06, SiO_2 3.01, H_2O 13.80, total 99.96%. Al content seems unusually high and it could be named aluminobetafite.

3099. (55) *Gadolinite from Hazu-machi, Aichi Prefecture, Japan.* p. 1220.

A greenish black crystal of gadolinite, 1.0 cm. across, was collected with allanite from a pegmatite of hornblende-biotite-granite at Sakiyama, Hazu-machi. Chemical analysis gave BeO 9.10, MgO 0.61, CaO 1.08, MnO 6.80, FeO 11.45, Al_2O_3 1.49, Fe_2O_3 5.56, Ce_2O_3 2.73, ΣY_2O_3

30.33, ThO_2 4.26, SiO_2 23.85, $H_2O(-)$ 0.94, $H_2O(+)$ 2.67, total 100.87%.

3100. (56) *On the allanite from Daibosatsu Pass, Yamanashi Prefecture, Japan.* p. 1238.

Prismatic crystals of allanite, 5×1×0.5 cm., elongated along c-axis were found in the central part of pegmatitic veins that are distributed in strongly hydrothermally altered sandstone or shale covering the area. Observed crystal forms are $a\{100\}$, $c\{001\}$, $m\{110\}$ and $r(\bar{1}01)$. Sp. gr. 4.3. Chemical analysis gave SiO_2 29.92, P_2O_5 tr., TiO_2 0.88, ZrO_2 0.26, ThO_2 1.05, SnO tr., MgO 0.64, CaO 10.43, Ce_2O_3 9.45, La_2O_3 4.29, other rare-earths 8.35, Na_2O 0.22, K_2O 0.41, U_3O_8 0.03, SrO 0.01, MnO 1.06, BeO 0.35, Al_2O_3 13.56, Fe_2O_3 5.96, FeO 11.13, H_2O (−) 0.08, $H_2O(+)$ 2.05, total 100.13%.

3101. **Misumi (Seizo) and Ide (Yasushi):** *Chemical investigations of the minerals containing rarer elements from Kyushu. Allanites from Uchino-mura and Kojima-mura, Fukuoka Prefecture, Japan.* Nippon Kagaku Zasshi, **81**, 1349–1350 (1960). (in Japanese.)

A dark brownish allanite, sp. gr. 3.75, was found in pegmatite at Urata associated with zircon, xenotime and monazite. Chemical analysis gave MgO 0.02, CaO 11.49, MnO 0.86, FeO 11.59, Fe_2O_3 3.49, Al_2O_3 15.56, Ce_2O_3 6.60, ΣLa_2O_3 7.49, ΣY_2O_3 6.28, ThO_2 1.95, SiO_2 31.42, H_2O 3.56, total 100.31%.

Prismatic allanite from pegmatite at Kofuji occurs with zircon and monazite. Sp. gr., 3.76 at 22°C. Observed crystal forms are $c\{001\}$, $a\{110\}$, $r\{\bar{1}01\}$, $i\{\bar{1}02\}$ and $m\{110\}$. Chemical analysis gave MgO 0.05, CaO 10.15, MnO 1.46, FeO 11.49, Fe_2O_3 5.24, Al_2O_3 16.14, Ce_2O_3 9.12, ΣLa_2O_3 5.20, ΣY_2O_3 4.65, ThO_2 1.79, SiO_2 31.30, H_2O 2.53, total 99.12%.

3102. **Yoshimura (Toyofumi) and Momoi (Hitoshi):** *Inesite from the Kacho mine, Kochi Prefecture.* Kobutsugaku Zasshi, **5**, 1–10, 4 figs. (1960). (in Japanese.)

Inesite crystals were found in the manganese deposits of the Kacho mine. $(-)2V=68°\sim73°$, $\alpha=1.616$ $\beta=1.639$ $\gamma=1.652$; $d(\frac{18}{1})=3.00$. The result of chemical analysis is as follows: SiO_2 43.67, Al_2O_3 0.34, Fe_2O_3 0.21, MnO 36.92, CaO 8.30, MgO 0.87, $H_2O(+)$ 5.96, $H_2O(-)$ 2.85, total 99.12%. The X-ray powder patterns and d. t. a. curves of the mineral are in good agreement with those from the other localities in Japan. Heating product was determined as bustamite by infra-red absorption and X-ray studies.

3103. **Miyahisa (Michitoshi), Tanaka (Nobuya) and Muta (Kunihiko):** *Datolite from the Obira mine, Ôita Prefecture, Japan.* Miner. Jour., **3**, 122–129, 1 pl., 1 fig. (1961).

Datolite of the Ginjiki deposit of the Obira mine is white to pale greenish white in colour and massive, occurring in association with skarn minerals. Refractive indices are: $\alpha=1.6273$, $\beta=1.652\sim1.655$, $\gamma=1.666$, and $(-)2V$ is $73°\pm1.5°$. The chemical composition is as follows;

SiO_2 37.64, Al_2O_3 0.32, FeO 0.22, MnO none, CaO 34.90, MgO 0.60, B_2O_3 21.31, $H_2O(+)$ 5.66, total 100.65%. Trace of Ge is also contained. When weathered, it alters to a clayey mineral and decreases in the B_2O_3 content. It is paragenetic with quartz, calcite, stilpnomelane and grunerite (?), and includes or replaces skarn minerals of earlier stage. Hence, it must have been formed under hydrothermal condition in a relatively later stage of mineralization.

3104. **Watanabe (Takeo), Kato (Akira) and Ito (Jun):** *Manganpyrosmalite from the Kyurazawa mine, Tochigi Prefecture.* Miner. Jour., **3**, 130–138, 2 figs. (1961).

Manganpyrosmalite $(Mn, Fe)_8Si_6O_{15}(OH, Cl)_{10}$ occurs abundantly as ore forming mineral at the Shinsanjin ore body of the Kyurazawa mine, Tochigi Prefecture, Japan. The first occurrence of pyrosmalite in Japan has been reported from another ore body of the same mine. The chemical analysis of the newly found manganpyrosmalite by J. Ito gave SiO_2 35.43, FeO 9.57, MnO 42.01, MgO 1.14, Al_2O_3 0.50, Cl 5.00, SO_3 0.17, $H_2O(\pm)$ 7.50, $-O=Cl_2$ −1.13, total 100.19%. Sp. gr. 3.12, hardness $4\frac{1}{2}$; $\varepsilon=1.631$, $\omega=1.667$, $\omega-\varepsilon=0.036$, uniaxial negative; lattice constants measured from the X-ray powder pattern are $a_0=13.42$Å. and $c_0=7.159$Å. The associated minerals are rhodonite, manganese amphibole, garnet, mangancalcite, quartz and small amounts of sulphide minerals. The chemical analysis of previously reported pyrosmalite from the Odaki ore boody in this mine by H. Haramura came out as follows; SiO_2 33.50, TiO_2 0.08, Al_2O_3 0.11, Fe_2O_3 1.07, FeO 24.09, MnO 27.62, MgO 1.65, ZnO 0.04, CaO <0.02, $H_2O(-)$ 0.02, $H_2O(+)$ 6.53, P_2O_5 <0.02, Cl 5.63, $-O=Cl_2$ −1.27, total 99.31%. The correlation between the refractive indices and FeO contents of the minerals of friedelite–manganpyrosmalite–pyrosmalite series is given.

3105. **Masutomi (Kazunosuke), Nagashima (Kôzô) and Kato (Akira):** *Kobeite from the Ushio mine, Kyoto Prefecture, Japan and re-examination of kobeite.* Miner. Jour., **3**, 139–147, 2 figs. (1961).

A black prismatic kobeite-like mineral from a granite pegmatite of the Ushio mine in Ômiya town, Kyoto Prefecture and the kobeite from the original locality have been studied. Both the chemical analyses and the X-ray powder patterns of heated materials of the two minerals gave the concordant results. The two minerals contain notable amount of zirconium and after heat treatment give X-ray patterns similar to those of stabilized cubic zirconia.

Kobeite will not be a member of the euxenite-polycrase series but may be a distinct mineral species of multiple oxide containing Y, Fe, U, Ti, Zr andNb as the main components.

3106. **Hayashi (Shôichiro):** *Cosalite from the Hagidaira mine, Gun'ma Prefecture, Japan.* Miner.

Jour., 3, 148–155, 1 pl., 3 figs. (1961).

A new mode of occurrence of cosalite from Japan and its mineralogical properties are described. The mineral was identified by X-ray studies and chemical analyses. It occurs in a bedded type manganese deposit in a Palaeozoic formation. Acicular crystals were found in a vug of rhodonite with quartz or growing on the surface of quartz crystals. The cosalte is associated with such metallic minerals as gersdorffite, niccolite, huebnerite, scheelite, sphalerite, galena, pyrrhotite, uraninite, etc., as well as manganese minerals.

X-ray and crystallographic data, optical properties, etch tests and chemical analysis are presented. Cell constants: a_0=19.09Å., b_0=23.89Å. and c_0=4.058Å. Space group: D_{2h}^{16}-Pbnm.

3107. **Nambu (Matsuo), Okada (Kokichi) and Tanida (Katsutoshi):** *Psilomelane from the Miyazaki mine, Miyagi Prefecture.* Kobutsugaku Zasshi, **5**, 126–135, 5 figs. (1961). (in Japanese.)

Massive botryoidal manganese oxide from the Miyazaki mine was determined as psilomelane. Chemical analysis gives: MnO_2 63.65, MnO 7.29, Fe_2O_3 1.23, Al_2O_3 2.86, MgO 0.08, BaO 9.79, CaO 1.89, Na_2O 0.24, K_2O 0.82, SiO_2 4.32, $H_2O(+)$ 4.56, $H_2O(-)$ 2.90, total 99.63%, and the result is in good agreement with those obtained by Wadsley. The d. t. a. curves of the mineral have an exothermic peak at 670°C. and five endothermic peaks at 150°, 300°, 450°, 770° and 980°C. respectively. The X-ray powder patterns show that at 700°C. it transforms to hollandite and at 900°C. to hausmannite.

3108. **Shibuya (Gorô):** *On some blue schiller-feldspars.* Kobutsugaku Zasshi, **5**, 137–166, 10 figs. (1961). (in Japanese.)

Based upon the thermo-magnetic studies on four kinds of blue schiller-feldspars, discussions are given on the conditions of their formation and the cause of the schillerization. The specimens include exsolved opaque minerals having a common orientation parallel to crystallographic planes which show schillerization. These inclusions can be classified into several phases with different Ti contents of the system Fe_3O_4–Fe_2TiO_4 and they have residual magnetism along the common orientation. Number of the inclusions amounts to 10^4~10^5 per 1 mm³. of the host feldspar. Both the scattering by minute inclusions of the size of thousands of Ångströms and the reflection by those of bigger sizes may be the cause of the schillerization. A new solvus curve was proposed for the system Fe_3O_4–Fe_2TiO_4.

3109. **Fujii (Isao):** *On the distribution of the individual rare-earth elements in some rare-earth minerals from Japan, Korea and North-Eastern China.* Kobutsugaku Zasshi, **5**, 167–180 (1961). (in Japanese.)

Individual rere-earth elements in monazite, allanite, euxenite, fer-

gusonite, yttrialite, xenotime and gadolinite were determined using a new combined method of neutron activation analysis and ion-exchange resin Neotrin method. Very well established chemical procedures were described in detail. The distribution scheme of rare-earth elements obtained from the results shows close agreements to the one obtained by Semenov by X-ray fluorescence analysis on the similar minerals from Europe.

3110. **Haramura (Hiroshi):** *Notes on rock-forming minerals* (19). *Garnet in aplite from a quarry at Hirasawa in the Tsukuba district.* Jour. Geol. Soc. Jap., 67, 186–187 (1961).

Almandinous garnet from the aplite dike in the granite which was investigated in detail by K. Sugi (1930) was studied by the author mineralogically. He obtained the following results. Chemical composition: SiO_2 37.27, TiO_2 tr., Al_2O_3 20.98, Fe_2O_3 1.01, FeO 28.67, MnO 11.80, MgO 0.39, CaO tr., Na_2O 0.19, K_2O tr., $H_2O(+)$ tr., $H_2O(-)$ tr., P_2O_5 tr., rare earths tr., total 100.31%. $a_0=11.55$Å. Molecular composition: Sp. 28.92, Alm. 69.39, Pyr. 1.69, Gr. none, And. none. Pink to the naked eyes, colourless and isotropic under the microscope, less than 0.3 mm. in diameter. The host rock is composed of quartz, oligoclase, microcline, muscovite and the garnet.

3111. **Yoshimura (Toyofumi) and Momoi (Hitoshi):** *Dannemorite from Zômeki, Yamaguchi Prefecture, Japan.* Sc. Rept. Fac. Sc., Kyushu Univ., Geol., 5, 99–110, 2 figs. (1961). (Japanese with English abstract.)

The material examined were obtained from the Zômeki adit of Kusugi mine, occurring as long needles about 3 cm. long in quartz-rich portions of manganese deposits in the Palaeozoic chert and slate. They are accompanied by abundant grains of spessartine ($a_0=11.62$Å., $d=4.11$). The specific gravity measured by picnometer is 3.30 at 28°C. The optical properties are as follows: $\alpha=1.648$, $\beta=1.661$, $\gamma=1.672$, $c\wedge Z=19°$, $(-)2V=88°$. The chemical composition follows: SiO_2 51.34, Al_2O_3 1.44, Fe_2O_3 2.29, FeO 13.55, MnO 14.04, MgO 13.28, CaO 3.00, $H_2O(+)$ 1.06, $H_2O(-)$ 0.15, total 100.15%. It shows a remarkably high manganese content as a mineral of the cummingtonite group. The X-ray diffraction patterns are, however, in good accordance with those reported by Johansson.

New Minerals

3112. **Watanabe (Takeo), Takeuchi (Yoshio) and Ito (Jun):** *The minerals of the Noda-Tamagawa mine, Iwaté Prefecture, Japan.* III. *Yoshimuraite, a new barium-titanium-manganese silicate mineral.* Miner. Jour., 3, 156–167, 1 pl., 5 figs. (1961). [3004, 3026]

Yoshimuraite, a new barium-titanium-manganese complex silicate mineral, was found in an alkali-pegmatitic facies bordering the bedded manganese deposit of the Misago ore body of the Noda-Ta-

magawa mine. Yoshimuraite occurs as dark-brownish platy to tabular crystals, or sometimes in the stellate groups embedded in coarse aggregates of barium-bearing potash-feldspar, quartz, richterite, urbanite, rhodonite etc.

It resembles lamprophyllite and astrophyllite which usually occur in alkali-pegmatites. It is orange brown in colour, brittle and has a perfect cleavage parallel to {010} and distinct cleavages on {10$\bar{1}$} and {101}. Polysynthetic twinning {010} is common. Hardness, 4½; Sp. gr., 4.13 (obs.) and 4.21 (calc.). Triclinic, with $a_0=7.00$, $b_0=14.71$, $c_0=5.39$Å., $\alpha=93.5°$, $\beta=90.2°$, $\gamma=95.3°$, and $a:b:c=0.476:1:0.366$. Space group, $P\bar{1}$. Biaxial positive with $\alpha=1.763$, $\beta=1.777$, $\gamma=1.785$, $(+)2V=85°\sim90°$, $\rho>\upsilon$, and absorption $X<Y\leqq Z$. Optical orientation, γ' nearly parallel to c-axis, α' nearly parallel to a-axis. Pleochroism, α bright yellow, β orange-brown, γ brown.

Chemical analysis by J. Ito gave SiO_2 18.25, TiO_2 10.00, Fe_2O_3 1.32, FeO 1.47, MnO 17.64, MgO 0.56, ZnO 0.50, BaO 33.51, SrO 4.62, Na_2O 0.16, K_2O 0.03, P_2O_5 3.98, SO_3 5.40, Cl 0.41, $H_2O(\pm)$ 2.34, less for Cl 0.09, total 100.10%. The results indicate a formula of approximately X_2Y_2 (Ti, Fe)$O(Si_2O_7)[(P, S)O_4]$(OH) or $X_2Y_2(Ti, Fe)(SiO_4)_2[(P, S)_4]$(OH), where X=Ba, Sr and Na, Y=Mn, Fe, Mg and Zn.

The mineral is named after Professor Toyofumi Yoshimura who has contributed much to the study of manganese minerals in Japan.

Physical Properties of Minerals

3113. **Okada (Kokichi):** *Thermal studies on some todorokites.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., **45**, 49–53 (1961). (Japanese with English abstract.)

All the d. t. a. curves of todorokites from Todoroki, Fukaura, Maruyama, Hongo and Hamayokokawa mines show similar endothermic peak at 640~660°C. caused by conversion from todorokite to hausmannite.

Rock-forming Minerals and Petrology

3114. **Yashima (Ryuichi):** *Phenocryst pigeonite from Sengamori, Fukushima Prefecture.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., **45**, 9-13 (1961). (Japanese with English abstract.)

Pigeonites occur as phenocrysts with diopsidic augite, rhombic pyroxene, bytownite and olivine in andesitic basalt from a volcanic neck at Sengamori, Fukushima Prefecture. The crystallization course of pyroxenes is in good accordance with that of Skaergaard intrusion.

3115. **Suzuki (Jujin):** *Clinoptilolite in the tuff from Chita Peninsula, Aichi Prefecture.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., **45**, 14–16 (1961). (Japanese with English abstract.)

The tuff distributed in the southern part of Chita Peninsula, Aichi Prefecture, belongs to the Miocene sediments, in which clinoptilolite was found as an alteration product of an acidic volcanic glass. The clinoptiloloite is identified by

X-ray diffraction, d. t. a. and microscopic observation.

3116. **Seki (Yotarô):** *Jadeite from Kanasaki of the Kanto Mountains, Central Japan.* Jour. Geol. Soc. Jap., **67**, 101~104 (1961).

Jadeite from albitite in serpentinites of the Kanto Mountains was analyzed giving the following results: SiO_2 60. 03, Al_2O_3 22. 78, Fe_2O_3 0. 32, MnO 0. 11, MgO 1. 00, CaO 1. 14, Na_2O 13. 77, K_2O 0. 22, total 99. 37%. Optical properties: $\alpha=1.655\pm0.002$, $\beta=1.659\pm0.002$, $\gamma=1.669\pm0.002$, $(+)2V=69\sim71°$, $c\wedge Z=35°$, $\rho<\upsilon$ (strong). Muscovite, sodic plagioclase and titanite coexist with the jadeite in the rock.

3117. **Seki (Yotarô):** *Zoisite in altered gabbro of the Miyamori district, Iwaté Prefecture.* Jour. Geol. Soc. Jap., **67**, 143–146 (1961).

Zoisite from an altered hornblende gabbro of the Miyamori district was studied. Chemical composition: SiO_2 40. 31, Al_2O_3 33. 86, Fe_2O_3 0. 09, FeO 1. 05, MnO 0. 36, MgO 0. 70, CaO 22. 00, Na_2O n. d., K_2O n. d., $H_2O(+)$ 2. 10, $H_2O(-)$ 0. 48, total 100. 95%. It gives approximately the formula $Ca_4Al_5Si_6O_{25}(H_2O)$. The X-ray powder diffractogram is in good accordance with those for zoisites from other districts. Optical properties: $\alpha=1.701$, $\beta=1.703$, $\gamma=1.709$, $(-)2V=40\sim41°$, $\rho>\upsilon$, colourless in thin section, op. pl. $\perp$ (010), Sp. gr.=3. 31. The writer implies that the secondary alteration of the host gabbro is due to deuteric action accompanied by shear.

3118. **Karakida (Yoshifumi):** *Zircon overgrowths in the Ryôké metamorphic zone of the Yanai area, Southwest Japan.* Mem. Fac. Sci., Kyushu Univ., Ser. D, **10**, 59–72, 2 pls., 1 fig. (1961).

The Ryôké metamorphic terrain of the Yanai area, Southwest Japan, consists of non-metamorphozed zone, biotite schist zone, and banded gneiss zone, as well as the older Ryôké granodiorites and the younger Ryôké granites. Overgrowths are observed on the zircon crystals concentrated from granitized banded gneisses and granitic rocks of the Ryôké metamorphic terrain of the area. They are inferred to have been produced by mixing of sediments and granitic liquids and by the subsequent contamination of granitic magma, and the characteristic features of the overgrowths may indicate the specific conditions of mixing and contamination.

3119. **Yamaguchi (Masaru):** *Chrome-diopsides in the Horoman and Higashi-Akaishi peridotites, Japan.* Mem. Fac. Sc., Kyushu Univ., Ser. D, **10**, 233–245, 1 fig. (1961).

Green clino-pyroxene in the Horoman peridotite, Hokkaido, has been identified as chrome-diopside by optical, chemical, X-ray and infra-red absorption studies. For comparison, additional measurements were made on the chrome-diopside forming a vein in dunite from Higashi-Akaishi, Shikoku.

(1) Horoman chrome-diopside:

SiO_2 50.97, TiO_2 0.49, Al_2O_3 4.86, Fe_2O_3 0.92, Cr_2O_3 1.47, FeO 1.41, MnO 0.10, MgO 17.89, CaO 21.28, Na_2O 0.83, K_2O tr., $H_2O(+)$ 0.23, $H_2O(-)$ 0.07, total 100.52%; d=3.309; a_0=9.720, b_0=8.891, c_0=5.252Å., β=73°51', cell volume 435.9Å.^{3}; α=1.678~1.684, β=1.687~1.693, γ=1.697~1.703.

(2) Higashi-Akaishi chrome-diopside: d=3.268; a_0=9.734, b_0=8.915, c_0=5.274Å., β=74°04', cell volume 440.1Å.^{3}; α=1.671~1.674, β=1.681~1.685, γ=1.704~1.706.

High alumina content and small cell volume of the Horoman chrome-diopside are worthy of notice in that there is a possibility of the presence of a small amount of OH ions substituting for O ions in the structure of chrome diopside.

Topographical Mineralogy

3120. **Hayashi (Shôichiro) and Nagashima (Kôzô):** *A mineralogical note on the euxenite-polycrase series mineral from Syowa Base, Antarctica.* Antarctica Record, Repts. Jap. Antarctic Res. Exped., No. 11, 27-30, 1 fig. (1961). [3076]

A mineral with glassy lustre and conchoidal fracture from Showa Base was determined as a member of euxenite-polycrase series by X-ray and d. t. a. studies. The result of chemical analysis is as follows: MnO 0.05, Fe_2O_3 1.07, CaO 0.64, MgO 0.22, ΣCe_2O_3 0.38, ΣY_2O_3 25.26, ThO_2 3.20, UO_2 11.48, UO_3 0.67, $(Nb, Ta)_2O_5$ 30.76, TiO_2 24.74, SiO_2 0.33, SnO_2 0.11, $H_2O(+)$ 0.23, total 99.14%.

3121. **Minami (Eiichi), Ossaka (Jôyo) and Nakamura (Tadaharu):** *Garnet from East Ongul Island in the Antarctic Region.* Antarctica Record, Repts. Jap. Antarctic Res. Exped., No. 11, 31-35 (1961). (Japanese with English abstract.)

Reddish brown garnet crystals as large as 10×10×45 mm. were collected by Torii from East Ongul Island. Sp. gr. 3.954±0.005, a_0=11.530Å., n_{Na}=1.773±0.002. Chemical composition follows: SiO_2 40.02, Al_2O_3 21.90, Fe_2O_3 1.53, FeO 21.34, CaO 5.20, MgO 8.94, K_2O 0.01, Na_2O 0.06, $H_2O(-)$ 0.18, TiO_2 0.06, P_2O_5 0.00, MnO 0.93, SrO 0.00, total 100.17%, F 0.002%. Rb and Li were detected spectroscopically, but Cr and other rare elements were not. Molecular composition: Alm. 47.64, And. 4.59, Pyr. 35.49, Gr. 10.10, Sp. 2.18%.

Various Topics

3122. **Miyashiro (Akiho):** *Thermodynamics of reactions of rock-forming minerals with silica.* Jap. Jour. Geol. & Geogr., **31**, (I) 71-78, (II) 79-84, (III) 107-111, (IV) 113-120, (V) 241-246, (VI) 247-252 (1960).

The Gibbs free energies of reaction of minerals with one mole of quartz are proved to be useful as a measure of the mineral sequence which takes place with advancing degree of silica-undersaturation in an environment (Part I). Approximation formulas of describing the variations in breakdown temperatures of a mineral

in relation to varying degree of the silica-saturation are derived (Part II). By using these formulas equilibrium P, T-curves for various decomposition reactions of muscovite and phlogopite are calculated. In view of the results obtained stability of muscovite and biotite in igneous and metamorphic rocks are discussed (Parts IV & V). For an open system with regard to silica the chemical potential of silica is introduced as a convenient measure of the degree of silica-saturation, and the method is applied to calcite-wollastonite equilibrium (Part VI). Existing thermochemical data pertinent to these problems are reviewed (Part I), and the heat of formation for andalusite (or sillimanite) is newly estimated in the light of field evidences (Part III).

ABSTRACTORS

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